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Patrick A. Mattie

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PERFORMANCE PROPERTIES OF A TRANSLUCENT, X-RAY OPAQUE DENTAL ACRYLIC RESIN

Patrick Alan Mattie

APPROVED:

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Supervising Professor

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12-14-93
Date

APPROVED:

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Sanford A. Miller, Ph.D
Dean

PERFORMANCE PROPERTIES OF A TRANSLUCENT, X-RAY OPAQUE

DENTAL ACRYLIC RESIN

A

THESIS

Presented to the Faculty of

The University of Texas Graduate School of Biomedical Sciences

at San Antonio

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

By

Patrick A. Mattie, B.S., D.D.S.

San Antonio, Texas

June, 1995

DEDICATION

All my efforts are dedicated to my best friend, constant supporter and wife, Christina.

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PERFORMANCE PROPERTIES OF A TRANSLUCENT, X-RAY OPAQUE

DENTAL ACRYLIC RESIN

Patrick A. Mattie, M.S.

The University of Texas Graduate School of Biomedical Sciences

at San Antonio

Supervising Professor: Henry R. Rawls, Ph.D

Dental acrylic resins routinely used today are radiolucent and cannot be imaged using standard radiographic techniques. A significant number of foreign bodies are dental objects made from acrylic resin and, due to their radiolucency, are difficult to detect and remove. Delays in localizing or removing foreign bodies have lead to many injuries and deaths. Many authors and the American Dental Association have called for the development of radiopaque dental resins. Development of a radiopaque dental acrylic resin would provide an increased margin of safety for many

millions of dental patients.

The addition of high atomic number elements is required to provide radiopacity to acrylic resins. An acceptable radiopaque additive should be biocompatible and provide a useful level of radiopacity without significantly deteriorating important performance properties. Additives previously tested do not meet all standards of biocompatibility, esthetic requirements and performance properties, including radiopacity. Most additives weaken the resin or produce unesthetic optical properties. Only one acrylic resin with radiopaque properties is currently available in this country (Alike™, provisional crown and bridge resin) and provides only minimal radiopacity.

Triphenyl bismuth (TPB), soluble in a wide range of polymers, has been shown to provide adequate radiopacity without significantly altering transverse deflection. Cytotoxicity testing indicates it has a high level of biocompatibility. The ability to form a homogeneous acrylic resin appears to overcome the more serious of the problems exhibited by previous additives.

The purpose of this study was to assess the radiopacity and investigate the effects on physical properties of dental acrylic resin following incorporation of triphenyl bismuth. Methods to improve triphenyl bismuth-containing resin microbeads were also investigated. Triphenyl bismuth was incorporated into polymethyl methacrylate powder at five different concentrations, ranging from zero (control) to 40% by wt of powder. Heat- and self-cured samples were made from each of the five resin groups. For

comparison, samples made from Lucitone™, Alike™ and Jet Acrylic™ resins were also tested. Radiopacity of all samples was compared to that of aluminum as outlined in International Standards Organization Specification #4049. Seven physical performance properties were evaluated according to American Dental Association Specification #12 for denture base polymers.

Results showed that triphenyl bismuth can be homogeneously incorporated into polymethyl methacrylate at levels that provide a diagnostically useful range of radiopacities. At the lower end of this range, triphenyl bismuth does not significantly alter esthetic optical properties, polishability, packing plasticity, color stability or water sorption. Although it decreases the flexibility of self-cured specimens, TPB does not effect heat-cured specimens in this way. Solubility of self-cured specimens was the only performance standard not met or exceeded.

As triphenyl bismuth concentration increased, the amount of retained air, related to decreased resin viscosity and the presence of crystals of undissolved TPB, also increased. This resulted in stress concentrations and increased frequency of specimen breakage.

While the properties of the resin system tested in this study approach those of commercially acceptable acrylic resins, minor modifications are required in order to overcome problems with entrained air.

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I. INTRODUCTION

Acrylic resin dental prostheses that are accidentally ingested, aspirated or impacted during injury would be more easily and safely located if they were radiopaque. Acrylic polymers traditionally used in dentistry are radiolucent and cannot be imaged using routine radiographic techniques. Attempts to locate and remove a radiolucent dental prosthesis is very difficult and time-consuming, requiring advanced imaging procedures or surgical intervention. Significant delays can be life-threatening to the patient. Previous attempts at providing radiopacity have resulted in acrylic resins that are deficient in various physical and mechanical properties. This research project evaluated several performance properties of an experimental acrylic resin, made radiopaque by the addition of triphenyl bismuth (TPB). Radiopacity was compared to that of aluminum.

Although not a common occurrence, foreign bodies of dental origin are not rare (Chandler, 1971). McArthur and Taylor (1975) said that 40 deaths per year can be expected from such accidents. Foreign objects often pass through the gastrointestinal tract without problem. Objects aspirated into the tracheobronchial tree cannot be passed and can lead to airway obstruction and death. Death rates as high as 10% have been reported from aspiration of dental foreign bodies (Newton, 1987). If dental acrylic resins were radiopaque, location and removal would be much easier and safer. The American Dental Association Council on Dental

Materials, Instruments and Equipment has encouraged the development of radiopaque dental resins.

Presently, only one radiopaque provisional crown material (Alike™) is commercially available. Previous attempts at providing radiopacity have utilized mixtures of metals or radiopaque glasses with acrylic resins. However, esthetics and physical properties were unacceptable. Heavy metal salts such as barium or bismuth halides also failed due to poor esthetics, excessive solubility of the additive or poor strength (Chandler, 1971). In a preliminary evaluation, triphenyl bismuth, which is soluble in a wide range of polymers, was shown to form a homogeneous acrylic resin and provide adequate radiopacity without significantly altering transverse deflection (Rawls, 1990). TPB was also found to have a low order of cytotoxicity (Rawls et al., 1992), indicating that it is adequately biocompatible.

The purpose of this investigation was to assess the radiopacity and determine the effects on physical properties of dental acrylic resin following incorporation of TPB. Experimental groups containing four different concentrations of TPB were tested for radiopacity and physical properties. One control group, polymethyl methacrylate (PMMA) powder subjected to the same TPB incorporation process (but without TPB) was also tested. Heat processed and auto-polymerized samples were made from each of the four experimental groups and the control group. For comparison, Lucitone™, a commercial heat processed denture base resin, Alike™, an autopolymerizing, radiopaque provisional restoration material

and Jet Acrylic™ provisional resin, was also tested. Radiopacity was evaluated according to I.S.O. Specification #4049. Physical and mechanical properties were evaluated according to A.D.A. Specification #12 for denture base polymers.

Our working hypothesis is that triphenyl bismuth can be incorporated into dental acrylic resin and result in radiopacity adequate for medical detection without adversely effecting mechanical, physical or processing properties.

II. LITERATURE REVIEW

A. Denture Base Materials

Before 1840, naturally occurring materials were used for denture bases. Hard wood, ivory, and bone with natural teeth held in place by screws were common before 1800. Many of the other basic dental materials including gold, amalgam, wax and plaster were available almost 100 years before an acceptable dental resin was developed (Peyton, 1975).

"Vulcanite" was introduced to dentistry about 1855 after Charles Goodyear developed the process to vulcanize rubber. Vulcanite, in combination with porcelain teeth, became the standard of the profession for treating denture patients for over 75 years. Unfortunately, inert materials added to characterize the naturally opaque, olive brown color did not overcome esthetic problems and also decreased the material's strength (Winkler, 1984). The gradual development of synthetic resin materials made vulcanite obsolete by 1940.

John Wesley Hyatt in 1868 developed "celluloid", a cellulose nitrate, the first organic plastic molding compound. Though more esthetic than vulcanite, patients objected to the odor and taste of camphor, which was added to plasticize the material. Other cellulose containing compounds used until 1930 had dimensional stability problems that prevented their popular use.

"Bakelite" and other phenol-formaldehyde resins were used from 1930 until 1940. The quality of the dentures was very sensitive to

processing techniques and was the major drawback to this material. Many commercial resin products were developed from 1930 to 1940. Attempts to adapt them for dental use were characterized by inadequate esthetics, dimensional instability, brittleness or color changes.

Vernonite, the first acrylic resin used in dentistry was introduced by Dr's. Harold and Lester Vernon in 1937. Many other dental acrylic resins quickly followed and were so successful that by 1946, 95% of all dentures were made of polymers or copolymers of methyl methacrylate (Winkler, 1984). The universal use of acrylic resins is the result of their overall impressive physical properties. They have excellent esthetics, adequate dimensional stability and strength, as well as low water sorption, solubility and toxicity. The handling properties are good and allow simple molding and processing techniques. Most denture base materials used today are polymers of methyl methacrylate.

Recent developments include light activated denture resins, high impact strength materials using butadiene-styrene rubber reinforcement and microwave activated materials (Craig, 1989).

B. Modern Acrylic Resins

Acrylic resins are polymers of acrylic acid or methacrylic acid and their esters. They are used extensively in dentistry but have other applications including bone cement, hard contact lenses and Plexiglass™. Acrylic resins used in dentistry are primarily polymers of methyl methacrylate and are used in fabrication of

complete and partial dentures, artificial teeth, orthodontic appliances, provisional crowns and bridges, and customized impression trays.

Polymerization of the resin occurs by an addition reaction, initiated by benzoyl peroxide free radicals which attack the double bonds of acrylic monomers. The activated monomers initiate a chain-growing reaction that continues until most of the monomer is polymerized. Room temperature or self-cure resins require a chemical accelerator, most commonly an aromatic amine such as dimethyl-*p*-toluidine, to produce enough free radicals to drive the polymerization reaction. Heat is the accelerator for heat-processed denture base resins, decomposing the benzoyl peroxide initiator fast enough without chemical accelerators. Inhibitors, usually hydroquinone, extend the shelf-life and working time of the monomer by acting as a scavenger of free-radicals, delaying polymerization until the inhibitor is depleted.

Commercial resins are generally used as two component systems, a powder and liquid. The liquid contains the monomer and inhibitor. Cross-linking agents, usually glycol dimethacrylate, may be added to increase hardness and craze resistance. Plasticizers such as dibutyl phthalate can be added to produce a more resilient, softer material. Self-cure or autopolymerizing resins are essentially identical except for the addition of a chemical accelerator to the liquid.

The powder component contains the benzoyl peroxide initiator and the polymer powder, usually spherical beads of polymethyl

methacrylate. Inorganic pigment tints and fibers are also usually added.

Impact-resistant copolymers, e.g., methylmethacrylate-butadiene, have been developed to reduce the brittle nature of dental acrylics resins.

Heat-activated resins have the higher transverse deflection strengths, are more color stable, contain less residual unreacted monomer and are the material of choice for fabricating dentures (Winkler, 1984). The amine accelerators are responsible for the color instability of autopolymerizing resins. Incomplete curing results in excess residual monomer. This plasticizes the resin, making it weaker and dimensionally unstable and can lead to oral tissue irritation.

Light-cured acrylics, Triad™, (Dentsply International, York, PA) are cured in a process similar to light-cured composites. The material, supplied as sheets of resin dough, is polymerized in a special curing unit under high intensity quartz-halogen lamps. Rather that PMMA, Tirad™ consists of a urethane dimethacrylate with a small amount of microfine silica added to improve handling properties. This material has been used for fabricating impression trays, denture bases, orthodontic appliances and as a repair material (Fellman, 1989). Its most unique use is as a directly applied denture reline material. Biological testing has shown the material to be non-toxic (Ogle et al., 1986). Early problems with flexural strength and internal surface detail have been improved (Tan et al., 1989).

C. Denture Foreign Bodies

1. Incidence

The radiolucency of dental resins has been shown to significantly increase the hazards associated with dental foreign bodies (Tamura et al., 1986). Reliable data on the incidence of aspirated or ingested dental acrylic resin is not available. Though not common, many reports of dental foreign bodies have been made in the literature and can be used as a rough estimate. Certainly, many such events go unreported, but dental objects, including fragments or whole appliances, are estimated to account for 3-8% of all foreign bodies. Many of the patients require hospitalization and/or advanced imaging techniques or invasive procedures to help localize and remove the objects. One large study found 59% of in-patient cases involved foreign bodies of dental origin (Chandler et al., 1971a).

The large numbers of patients receiving prosthodontic care (Lang, 1990) suggests that the incidence of foreign bodies and the need to locate them will not likely diminish. The most commonly ingested or aspirated prosthesis is a maxillary partial denture replacing a few anterior teeth, or an ill-fitting or fractured appliance (Chandler et al., 1971a). Conditions that diminish a patient's protective reflexes, including intoxication, epileptic seizures or unconsciousness during sleep or following trauma may contribute to the incidence (Brauer, 1981). Bunker and Aberdeen (1962) and Donaldson et al. (1971) stressed the importance of patient education in the maintenance and repair of faulty dentures. The

South Dakota State Dental Association formed a committee in 1961 to develop a patient education pamphlet, warning of the increased hazards of foreign bodies in denture patients.

2. Ingested Dentures

Swallowed objects often pass unnoticed through the gastrointestinal tract (Furste and Watkins, 1959). They may, however, cause obstructions, abscesses, perforations or hemorrhage even after long asymptomatic periods (Bloodworth and Kenner, 1992).

Turner (1947) reported on a 52 year old patient who swallowed her partial denture while eating. Clinical and radiographic examinations failed to detect the presence of the prosthesis until 15 years later when it was removed to treat dysphagia. Singleton and Richards (1967) described a case of tracheo-esophageal fistula resulting from swallowing of a partial denture four years previously. They made a plea for resins with radiopaque agents as the appliance in this case was not detectable radiographically. Many other authors including Drinnan (1967), Perenack (1980) and Hazelrigg (1984) have described similar cases of partial and complete denture ingestion.

Sherman et al. (1968) and Sarginson (1991) wrote of the deaths of two patients after swallowing dentures, even though hospitalized and treated appropriately.

3. Dentures as Airway Hazards

Aspirated objects are much more dangerous, requiring immediate

localization and removal (Schneider and Roistacher 1971). Donaldson et al. (1971) wrote that death may result from asphyxia or cardiac arrest. Aspiration can lead to bronchospasm, laryngospasm or total obstruction of the airway. Potential vagal inhibition may result in cardiac arrest. They also stated that altered levels of consciousness increased the likelihood of such hazards.

Ginsburg (1928) wrote that any object not removed from the airway will eventually be fatal. Chandler et al. (1971a) reported deaths in 10% of 123 cases involving aspiration of dental prosthetic materials. Adelman (1988) reported on three deaths due to aspiration of dental appliances and stated that radiopacity would aid in diagnosis. Littner et al. (1982) reported several cases of dental foreign bodies and called for all dental materials and instruments to be radiopaque for purposes of identification and detection.

4. Traumatic Impaction

Impaction of appliances following traumatic injury presents a particularly difficult problem in that the patient may be unconscious and unable to help in diagnosis (Brauer, 1981). Treatment of traumatic injuries can be more complicated in patients who wear radiolucent prostheses. Bloodworth and Render (1992) concluded from their survey of oral surgery and emergency medicine services that the problem is significant enough to warrant the development of radiopaque denture resins.

D. Detection Problems

Materials that are radiopaque are much easier to detect and localize. This is especially important when the patient does not know or is not conscious to report whether the object was swallowed or aspirated. Many attempts to detect radiolucent dental appliances using standard radiographic techniques have failed with potentially hazardous results for the patient (Craig (1954), Banham (1965) and Drinnan (1967).

Bloodworth and Render (1992) found that lack of radiopacity significantly decreases diagnostic abilities. Kerr (1966) reported on 15 cases involving swallowed dentures between 1960 and 1964. He stressed the radiologist's problems in detecting acrylic resin. Barium sulfate used by radiologists as a contrast medium does not easily adhere to acrylic resin and is unreliable. Banham (1965) reported 2 cases of a swallowed denture lodged in the patients' esophagus. In both cases, radiologists reported "no foreign body" when reading radiographs taken with a barium swallow.

Newton et al. (1987) evaluated computed tomography (CT) as a means to detect radiolucent denture resins. They found CT could detect radiolucent samples as small as 10 mm by 1.5 mm. Detection would be more difficult if located in a collapsed lung. Hurst et al. (1977) reported a major disadvantage to CT is the increased patient radiation exposure. Cost effectiveness and availability would also be problems in using CT.

E. Radiopaque Additives

Incorporation of high atomic number additives are required in order to impart radiopacity to acrylic resin. Ideally, all intraoral devices or appliances should be radiopaque, just as most dental instruments and many restorative materials are. However, only one radiopaque acrylic resin is currently available (Alike™, GC-Coe Laboratories, Chicago,IL) and provides only minimal radiopacity (Mattie et al., 1993). It is used a a self-cure provisional crown and bridge material. No radiopaque denture base resin is currently available in the United States.

Radiopaque additives that previously were used were found to result in unacceptably diminished performance properties or failed to provide adequate radiopacity. An acceptable radiopaque dental resin should be biocompatible, provide a diagnostic level of radiopacity and not significantly deteriorate performance properties (Bursey and Webb, 1960).

F. Previously Tested Additives

1. Metals

Many metals have been incorporated into acrylic based denture materials in attempts to render them radiopaque. Saunsbury (1964) tried using 1% powdered amalgam but found it produced an unacceptable grey colored denture. Powdered aluminum, silver and copper decreased tensile strength as particle size and concentration of filler increased (Sehajpal and Sood, 1989). These and all other metal filler particles yield a non-homogeneous

structure that scatters light and deteriorates physical properties (Brauer, 1981). They produce stress concentrations at the filler particles, leaching of additives and air entrapment voids due to incomplete wetting by the monomer. These factors weaken the acrylic resin and may result in fracture (Sehajpal and Sood, 1989).

2. Inhomogeous Heavy Metal Compound Additives

Several inorganic metal salt additives have been tested for performance and radiopaque properties. Bismuth halides (trichloride and tribromide) when added beyond their solubility limits in the monomer, were found to impart excessive water absorption (Combe, 1972). Elzay (1971) tested dentures containing barium fluoride, barium sulfate and bismuth subnitrate. Esthetics of all three resins was unacceptable. Bismuth subnitrate and barium fluoride containing resins developed dark stains and barium sulfate caused excessive optical opacity.

The barium sulfate in Radiopaque™ (L.D. Caulk Co., Milford, DE) denture resin provided minimal radiopacity and was never marketed (Tsao et al., 1984). As levels of barium sulfate were increased to provide adequate radiopacity, transverse strength and resin translucency significantly decreased (Saunsbury, 1964 and Chang, 1981).

Barium fluoride is slightly water soluble and may be cytotoxic following prolonged exposure (Davy and Causton, 1982).

At least 8 different radiopaque glass fillers have been evaluated. Tensile strength and translucency decreased with higher filler content due to the non-homogenous structure (Chandler,

1971c). Molding was more difficult due to decreased flow and increased stickiness of the resin dough. Polishing was much more difficult and a high surface gloss could not be achieved (Chandler et al., 1971b,d and Abou-Tabl et al., 1983).

3. Homogeneous Radiopaque Polymers and Resins

Heavy metal compounds which can be solubilized to form a homogeneous molecular structure can overcome many of the physical property deficiencies of other additives (Smid et al., 1989). Early attempts using this strategy met with limited success but recent efforts look encouraging.

Methyl methacrylate copolymerized with barium acrylate gives significant radiopacity but weakens the resin. Iodobenzene acts as a plasticizer and decreases the color stability. Raypaque™ (Coe Laboratories), a radiopaque resin once used for provisional crown and bridge restorations, contained bismuth bromide but exhibited decreased transverse and impact strengths (Combe, 1971). A bromine-methacrylate denture base resin was developed in England but was toxic and is not commercially available (Price, 1991).

Smid et al. (1989) dissolved bismuth halides (trichloride and tribromide) and uranyl nitrate into methyl methacrylate, forming radiopaque transparent resins. The bismuth halides were water sensitive, developing a surface haze after short exposures to water. They also could not be cured at room temperature with commonly used amine accelerators.

Rawls et al. (1990a) tested PMMA resins containing solubilized bismuth trihalides as well as uranyl nitrate and zirconyl

dimethacrylate. The resin doughs had a rubbery nature making them more difficult to mold. Uranyl nitrate is toxic but the bismuth and zirconium resins showed a high level of biocompatibility. All could be formulated to provide radiopacity exceeding that of aluminum. However, the water absorption exceeded standards and the resin was slightly brittle. The latter two problems could likely be overcome by adding plasticizers and cross-linking agents (Smid et al., 1989).

Triphenyl bismuth (TPB), which is soluble in a variety of polymers, overcomes many of the problems of the trihalides and other additives (Cabasso and Smid, 1990). It does not react with amine accelerators, thus allowing curing at ambient temperatures. Resins polymerized with TPB are water insoluble and remain transparent after extended exposure to water (Delaviz et al., 1990).

Rawls et al. (1990b) incorporated TPB into PMMA polymer beads at 15% (by wt) and tested it in a self-cure resin system. Transverse deflection was found not to be significantly affected and radiopacity could be made to exceed that of aluminum. Also, it was predicted from cytotoxicity evaluations that TPB and TPB-resins would have a high level of biocompatbility (Rawls et al., 1992).

These encouraging results justify a thorough evaluation of TPB as a radiopacifying additive for dental acrylic resins.

III. METHODS AND MATERIALS

A. Experimental Overview

Polymethyl methacrylate (PMMA) resin specimens containing various levels of triphenyl bismuth (TPB), hereafter called TPB-resins, were evaluated for radiopacity and seven performance properties. TPB (Fluka Chemical Corp., Ronkonkoma, NY) was incorporated into PMMA (Polyscience, Inc., Warrington, PA) using an emulsion and solvent evaporation process. This process produces TPB-containing PMMA as solid beads, 5-150 μ in diameter (microbeads). Preliminary test results were used to determine minimal levels of TPB for adequate radiopacity and maximal levels of TPB that allowed acceptable material handling properties. For this range of properties, PMMA powders were prepared that contained 20%, 24%, 30% and 40% TPB (% by weight). These were combined with benzoyl peroxide initiator and mixed 2:1 with monomer to produce 13%, 16%, 20% and 27% TPB in the cured resin specimens. PMMA resin containing 0% TPB, which had been subjected to the same emulsion and solvent evaporation process, was used as a control.

The control resin (0% TPB) and all TPB-resins were used to make both heat-cured and self-cured test specimens.

For comparison, the following three commercial resins were also tested: (1) Alike™ (GC-Coe Laboratories, Chicago, IL) a self-cured radiopaque provisional restorative material and (2) Lucitone™ (Dentsply, York, PA), a widely used heat-processed denture base

resin. (3) Jet Acrylic™ (Lang Dental Mfg. Co., Chicago, IL) a commonly used self-cured provisional resin was used in one performance test only (packing test), rather than Alike™.

Performance properties were evaluated as described in American Dental Association Specification No. 12 for Denture Base Polymers (Council on Dental Materials and Devices, 1975). International Standards Organization specification No. 4049, used in previous studies (Davy and Causton, 1982; Cabasso and Smid, 1990; Rawls et al., 1990), was also used in this investigation to evaluate radiopacity. It establishes aluminum as the comparison standard for resin based dental filling materials.

B. TPB-Resin Formulation

TPB was incorporated into a chemical grade PMMA powder (solid PMMA microbeads) using the following emulsion and solvent evaporation process (Table 1).

Solution #1: At room temperature (23 ± 2°C), 12 g PMMA and 0-8 g TPB powder were dissolved into 150 ml methylene chloride (Lot # BD500, Baxter Healthcare Corp., McGaw Park, Ill.) using a small magnetic stirrer in an 800 ml glass beaker. The beaker was covered with aluminum foil to prevent solvent evaporation.

Solution #2: In a 4000 ml beaker, 1500 ml deionized water was warmed to 65 ± 5°C over a Corning Hot Plate (Model-PC 101, Corning Glass Works, Neware, NJ) while stirring with a large magnetic stirrer. 15 g of a suspending agent, polyvinyl alcohol (Elvanol™,

Table 1. TPB RESIN FORMULATION - SOLVENT/EVAPORATION PROCESS

Solution #1	Solution #2	TPB Additive /12 g PMMA	
		(%)	(g)
150 ml Methylene Chloride	1500 ml Water	0 (Control)	0
		20	3.0
12 g PMMA	15 g polyvinyl alcohol	24	3.8
0-8 g TPB	0.6 g SLS	30	5.15
	12 ml Tween-80™	40	8.0

Methylene Chloride (Baxter Healthcare Corp., McGaw Park, IL.)

PMMA = Polymethyl methacrylate, Mw = 75,000 (Polyscience, Inc., Warrington, PA.)

TPB = Triphenyl bismuth (Fluka Chemical Corp., Ronkonkoma, NY)

Tween-80™ = Polyoxyethylene (20) Sorbitan Mono-oleate (Fisher Scientific, Fair Lawn, NJ)

Polyvinyl alcohol = Elvanol 50-42™, partially hydrolyzed polyvinyl acetate (E.I. duPont de Nemours, Wilmington, DL.)

SLS = Sodium Lauryl Sulfate (Fisher Scientific, Fair Lawn, NJ)

Lot #401080 E.I. duPont de Nemours, Wilmington, DE) was slowly added over 2-3 minutes to the water and stirred until completely in solution (1-2 hours). Two surfactant emulsification aids, 12 ml Tween 80™ (Fisher Scientific, Fair Lawn, NJ) and 0.6 g sodium lauryl sulfate, (Fisher Scientific, Fair Lawn, NJ) were added to the water and stirred until dissolved. The water solution was then removed from the warming plate and allowed to cool to room temperature. While cooling, the water was stirred with a 7 cm diameter, 4-blade stainless-steel stirrer at 200 rpm. This and all subsequent high-speed stirring was done with the same propeller blade (#L 04370-02, Cole-Parmer Instrument Co., Chicago, Ill.) in a Model SL 2400 Sted Fast™ vertical stirrer (Fisher Scientific).

Solution #1 (methylene chloride/PMMA/TPB) was slowly added to room temperature solution #2 and the stirring speed was increased to 595 rpm. Aluminum foil covered the flask so as to prevent the CH_2Cl_2 from evaporating too rapidly. This minimizes microbead porosity. 1-2 cc Silwet L-7210™ copolymer surfactant (Union Carbide, Danbury, CT) was added to prevent excessive foaming. After 15 minutes, the stirring was slowed to 500 rpm and continued for 24 hours. During this time the PMMA-TPB microbeads precipitated and the traces of CH_2Cl_2 were removed.

Following stirring, the precipitated polymer beads were allowed to settle for 3-4 hours. The clear supernatant liquid was decanted and discarded. The remaining liquid and polymer beads were filtered using a 38μ metal sieve (#400, Newark Wire Cloth Co., Newark, NJ). The filtrate was rinsed with 400 cc of 50°C deionized

water and then stirred slowly for 30 minutes in 400 cc of 50°C water using a small magnetic stirrer. This filtration, rinsing and stirring process was repeated 3 more times to remove as much residual polyvinyl alcohol (PVA) and surfactant as possible from the surface of the polymer beads. This was essential in order to minimize a blanching effect from the hot-water curing bath.

After rinsing, the filtrate was placed in an electric drying oven at 55°C for 12-18 hours. The yield of TPB-resin from the above process ranged from 10 g of 0% TPB to 18 g of 40% TPB (i.e., 80-90% yield).

Approximately 100 g of resin at each additive level was made, blended and stored in separate plastic containers prior to making test specimens. This controlled for variability among individual batches of processed resin.

C. Specimens

Specimens were prepared as described below for evaluation of the following properties:

1. Transverse Deflection

At least 5 specimens (65 mm x 10 mm x 2.5 mm) of each resin type were subjected to a 3-point bend test. Table 2 describes the loading and observation schedule. Table 3 shows the limits of acceptable deflection at specified loads.

Table 2.   TRANSVERSE DEFLECTION - SCHEDULE OF LOADING

| Time | | Load | |
Min	Sec	Newtons	grams
0	00	14.71	1,500
0	30	14.71	1,500
1	00	19.61	2,000
1	30	19.61	2,000
2	00	24.52	2,500
2	30	24.52	2,500
3	00	29.42	3,000
3	30	29.42	3,000
4	00	34.32	3,500
4	30	34.32	3,500
5	00	39.22	4,000
5	30	39.22	4,000
6	00	44.13	4,500
6	30	44.13	4,500
7	00	49.03	5,000
7	30	49.03	5,000

Table 3.   TRANSVERSE DEFLECTION - ACCEPTABLE LIMITS

Load Increment		Deflection, mm*	
Newtons	grams	Minimum	Maximum
14.7 - 34.3	1,500 - 3,500	--	2.5
14.7 - 49.0	1,500 - 5,000	2.0	5.5

* Deflection refers to the additional delfection that occurs when the load is increased beyond the initial 1,500 g load.

2. Transparency & Translucency

Specimens used in the transverse deflection test were also used to evaluate optical properties of transparency and translucency.

3. Radiopacity

The above specimens were milled to a thickness of 2.0 mm and used to assess radiopacity relative to that of aluminum.

4. Polishability

Samples were polished using conventional methods. The degree of smoothness and surface gloss was subjectively determined.

5. Water Sorption / Solubility

Two or more 50 mm diameter disks were made from each resin type and tested for water sorption and resin solubility.

6. Color Stability

Following sorption/solubility testing, the resin disks were exposed to a 275-watt Suntanner Bulb™ sunlamp (General Electric Co., Cleveland, OH) for 24 hours. Color stability was subjectively measured by change in color.

7. Packing Plasticity

A 5 kg mass was used to press 8 g of resin (doughy packing consistency) between a glass slab and the surface of a perforated

brass die. Results were expressed as average depth of intrusion of resin into the holes. Because Alike™ contains $BaSO_4$ as its radiopaque additive, which may alter the rheology of the resin, Jet Acrylic™ was used as the commercial self-cure comparison resin for this test. Jet Acrylic™ contains no radiopaque additives and is a PMMA acrylic resin commonly used to fabricate provisional restorations.

D. Resin Mixing and Processing

Powder/liquid resin systems were mixed for specimen fabrication as described in Table 4. Benzoyl peroxide 70% (Aldrich Chemical Co., Milwaukee, WI), a polymerization initiator, was finely divided and blended into the control and TPB-resin microbeads prior to mixing with monomer. 1% benzoyl peroxide was added for self-cured specimens and 4% added for heat-cured specimens. Initiators were incorporated into the commercial polymers by the manufacturer.

For all resins, polymer was slowly added to the monomer in a glass beaker and hand spatulated using a metal cement spatula until the polymer was completely wetted by the monomer. To avoid excessive incorporation of air into the resin mass, hand spatulation was kept to a minimum. The beaker was kept covered with aluminum foil until ready for packing. The resin was considered ready for packing when it separated cleanly from the walls of the beaker. All mixing and packing was done at room temperature.

Table 4.   RESIN SPECIMEN FORMULATIONS

Powder (polymer)	Liquid (monomer)	Powder/ Liquid (by wt.)	% TPB in cured resin (by wt.)	Specimen type made & tested
0% TPB (control)	Self-cure: equal parts Biocryl™/MMA* Heat-cure: Lucitone™	2/1	0	heat-cured & self-cured
20% TPB	"	"	13	"
24% TPB	"	"	16	"
30% TPB	"	"	20	"
40% TPB	"	"	27	"
Alike™ powder/liquid per manufacture		3/1	--	self-cured
Ch Lucitone™ powder/liq. per manufacturer		2.1/1	--	heat-cured
Jet Acrylic™ powder/liq. per manufacturer (packing test only)		2/1	--	--

*Methyl Methacrylate Monomer, (Polyscience, Inc., Warrington, PA)

Biocryl Resin™ (Great Lakes Orthodontics, Tonawanda, NY) contains MMA and unknown quantities of other monomers and accelerator.

Alike™ (GC Coe Laboratories, Chicago, IL)

Ch Lucitone™ (Dentsply/York Division, York, PA)

Jet Acrylic™ (Lang Mfg. Co., Chicago, IL)

All specimens were compression molded by hand using a Hanau denture processing clamp (Hanau Engineering Co.).

All gypsum molds were formed in Varsity™ brass denture flasks (Hanau Engineering Co., Buffalo, NY). Alike™, Ch Lucitone™, and self-cured TPB-resin specimens were packed into molds lined with two coats of Orthodontic Resin Separator™ (Caulk/Dentsply, Milford, Del.). Molds for heat-cured TPB-resins were lined with 0.0005" Buffalo Tin Foil™ (Buffalo Dental Mfg.Co., Brooklyn, NY). A thin layer of Vaseline™ (Cheesbrough Ponds Inc., Greenwich, CT) was placed on gypsum mold surfaces to facilitate tin foil placement. Resin for heat-cured specimens was trial-packed one time using 4" X 4" polyethylene sheets. Excess resin was carefully removed from the periphery of the mold cavities prior to final closure of the flask. The mold cavities were initially over-filled and the flask closed very slowly over 8-10 minutes to ensure adequate packing pressure and complete filling of the mold.

Immediately after packing into the appropriate mold, heat-cured specimens were placed in a pre-heated Model L-2 Hanau Curing Unit™ (Hanau Engineering Co.) and cured according to the schedule described in Table 5. Processing temperatures used for TPB-resins were based on preliminary test results. At the end of the curing cycle, molds were removed from the water bath, cooled in room temperature air for 30 minutes, then immersed in water at 23 ± 10°C for 15 minutes. Specimens were then retrieved from the mold.

Self-cured specimens were packed at room temperature and without trial packing.

Table 5.   CURING SCHEDULE - HEAT PROCESSED SPECIMENS

Specimen	Stage 1		Stage 2	
Type	Temp(°C)	Time(min)	Temp(°C)	Time(min)
Lucitone™	74	90	100	30
0% TPB	74	90	100	30
13% TPB	84	90	100	30
16% TPB	84	90	100	30
20% TPB	95	90	100	30
27% TPB	95	90	100	30

E. Specimen Fabrication

1. Transverse Deflection Specimens

Samples for the 3-point bend test were processed in an oversized gypsum mold (Plate 1). The mold cavity was slightly oversized to allow for polymerization and thermal shrinkage of the acrylic resin. Following processing, the specimens were mounted in a specially designed aluminum vice (Plate 2) and ground by hand, starting with #240 grit and ending with #600 grit emory paper, on a Handimet Grinder™ (#66799 Buehler LTD, Evanston, IL) to the following dimensions: 65.0 ± 0.5 mm x 10.00 ± 0.03 mm x 2.50 ± 0.03 mm. All grinding was done using copious water irrigation to prevent overheating of the resin. The prepared specimens were stored in deionized water at 37 ± 2°C for 50 ± 2 hours prior to testing.

At least 5 self-cured and 5 heat-cured specimens of each resin type were made and tested.

2. Transparency & Translucency

Specimens made for transverse deflection testing were also evaluated for optical properties of transparency and translucency.

3. Radiopacity

Following transparency and translucency tests, one specimen of each resin type was machined to a thickness of 2.0 ± 0.3 mm using the Handimet Grinder™ and used to test radiopacity.

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Plate 1. Gypsum mold used to fabricate specimens for transverse deflection, transparency, translucency and radiopacity tests. Cavities measure 67mm x 12mm x 3mm.

Plate 2. Aluminum vice used to hold resin specimens during grinding.

4. Polishability

Following radiopacity tests, the specimens were subjected to conventional polishing methods. Coarse Pumice, USP and Flower of Pumice, USP (Mayco Industries Inc., Philadelphia, PA) were used with rag wheels mounted on a Redwing™ lathe, Model #26A (Handle Mfg. Co. Inc., Westfield, NJ).

5. Water Sorption / Solubility

Disks 50 ± 1 mm in diameter and 0.5 ± 0.05 mm thick were made and used in water sorption and resin solubility tests. Two or more disks of each resin and processing type were made and tested.

Self-cured specimens were processed in a stainless steel mold 50 mm in diameter and 0.87 mm deep (Plate 3, Figure 1) and formed against a 5 mm thick steel plate.

A stainless steel-gypsum mold, also 50 mm in diameter and 0.87 mm deep (Plate 4, Figure 2) was used to form heat-cured test specimens.

Following processing, specimens were ground to the prescribed dimensions using the Handimet Grinder™. A brass specimen retainer and stainless steel retainer guide (Plate 5, Figure 3) were used to hold the samples during the grinding process. 10 lbs of vacuum applied through the brass retainer to the top of the specimen assisted in obtaining smooth, flat specimens of uniform thickness.

In order to calculate surface area, the average thickness and diameter of each specimen was determined. Specimens were dried in a desiccator (Plate 6) containing anhydrous calcium sulfate ($CaSO_4$)

32

Plate 3. Stainless steel mold used to fabricate self-cured specimens for sorption, solubility and color stability tests.

33

Figure 1.   Dimensions of stainless steel mold used to fabricate self-cure specimens for sorption, solubility and color stability tests.   All dimensions in mm.

MOLD FORMING PLATE

50

51

56

66

72

100-DIA

50-DIA

0.87 ±0.05

7.5

34
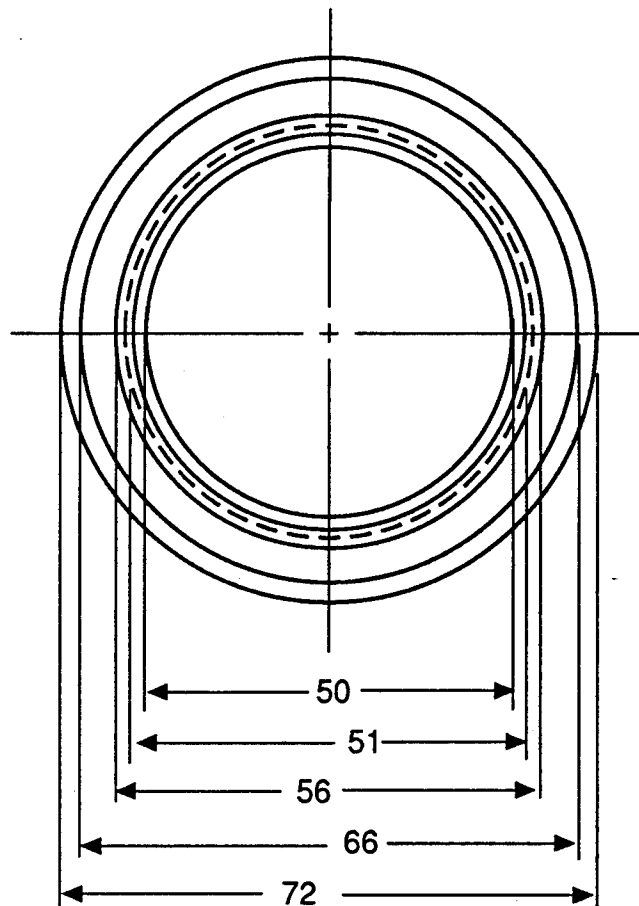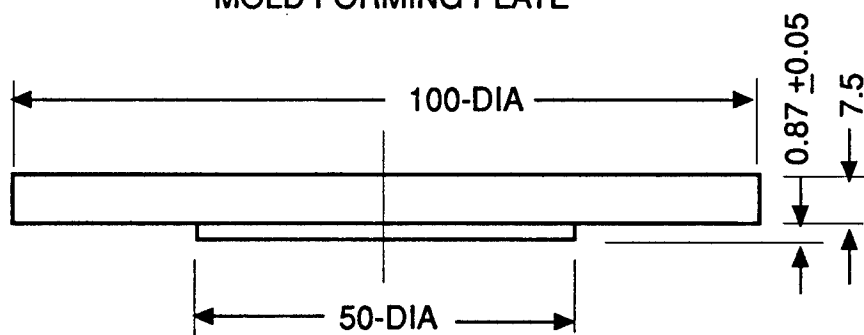
Plate 4. Stainless steel/gypsum mold used to fabricate heat-cured specimens for sorption, solubility and color stability tests.

35

Figure 2. System for forming sorption/solubility disks from heat-cured resins. A, mold forming ring; B, mold forming plate; C, upper half of denture flask; D, lower half of denture flask; E, specimen. Mold forming ring and plate made of stainless steel. All dimensions in millimeters.
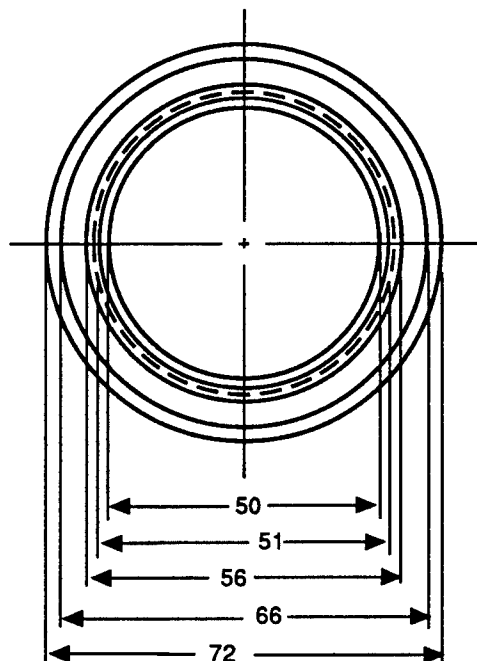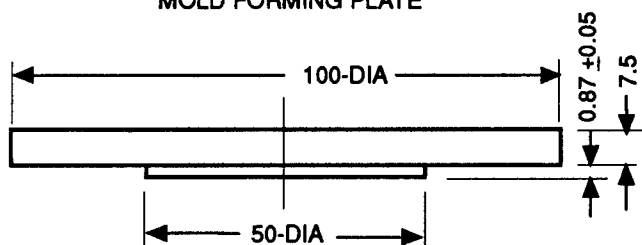
ASSEMBLY FOR FORMING THE
SPECIMEN MOLD CAVITY

C

A

GYPSUM

A

C

7.5

B
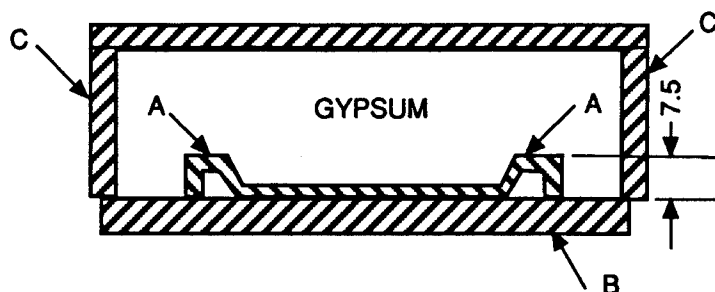
FORMATION OF THE SPECIMEN

D

E

A

A

C

GYPSUM

C

50

51

56

66

72

MOLD FORMING PLATE

100-DIA

0.87 ±0.05

7.5

50-DIA
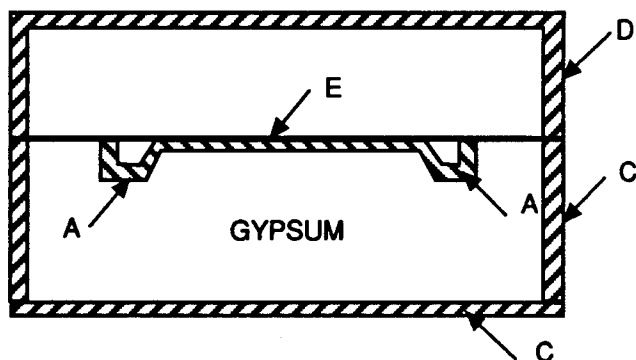
Plate 5.   Brass specimen retainer and guide used to hold acrylic disks during hand grinding.

Figure 3. Dimensions of assembly for holding sorption/solubility specimens during reduction to proper thickness. Specimen retainer made of brass. Retainer made of stainless steel. All dimensions in millimeters.

SPECIMEN RETAINER

RETAINER GUIDE

76

49.9

A   A

B   B

3mm DRILL

15R

DRILL No. 37
4 HOLES

76.4

6.4

15.5

12.5

35.5

46.0°

49.5

36

SECTION A-A

SECTION B-B

A-A
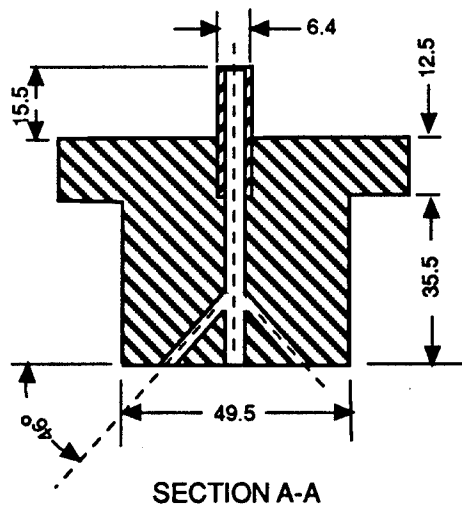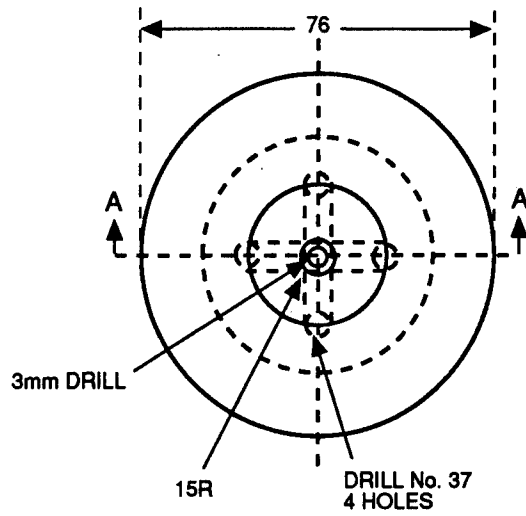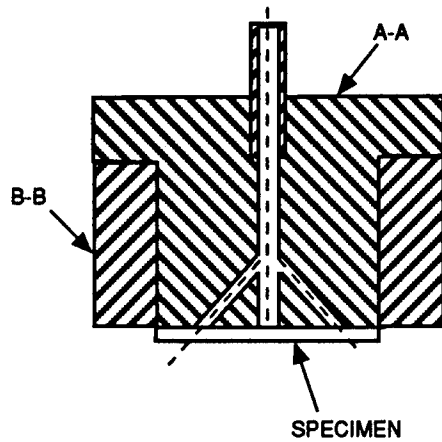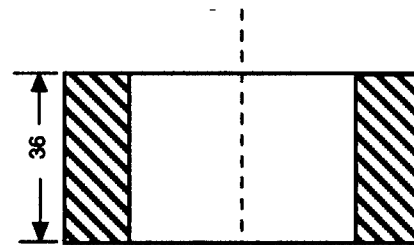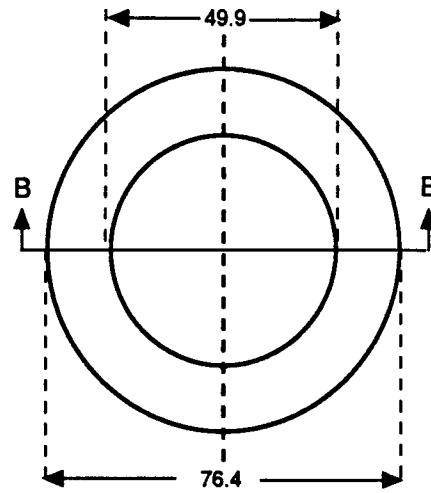
B-B

ALL DIMENSIONS IN mm

ASSEMBLY FOR REDUCING
THICKNESS OF SPECIMEN

SPECIMEN

38

Plate 6. Desiccator used to store specimens during sorption/ solubility tests.

at 37 ± 1°C for 24 hours, cooled to room temperature for one hour, then weighed to within 0.2 mg.

6. Color Stability

The same samples used for sorption/solubility tests were used to determine color stability.

F. Specimen Testing

A summary of test parameters and standards are shown in Table 6.

1. Transverse Deflection Test

Transverse deflection specimens were kept in 37°C water for 50 ± 2 hours prior to testing. A variable-strain mechanical tester (Instron™ Model #1125, Canton, MA) was used for 3-point bend tests. Specimens were centered between two, 3.2 mm diameter cylindrical supports, spaced 50 ± 0.025 mm apart. The supports with specimen were positioned to allow the loading nose to contact the center of the specimen (Plate 7). An initial load of 1,500 g was applied to the specimen and held for 30 seconds. An additional 500 g was applied over the next 30 seconds and held for 30 seconds. This schedule of loading in 500 g increments continued until a maximum 5,000 g load was applied or until the sample fractured.

Five or more specimens were tested for each resin type. Deflections were recorded at each 500 g load interval to the nearest 0.1 mm.

Table 6. PERFORMANCE EVALUATIONS AND STANDARDS

Test Parameter	Standard
Transverse Deflection	1.5 - 3.5 kg: ≤2.5mm 1.5 - 5.0 kg: 2.0-5.5mm
Transparency	Able to read 17 pitch print through the resin specimen
Translucency	Shadow of 10mm disk is visible through the specimen
Radiopacity	X-ray opacity equal to or greater than aluminum
Solubility	≤ 0.04 mg/cm^2
Water Sorption	≤ 0.8 mg/cm^2
Color Stability	No more than slight change in color
Polishability	Smooth, high gloss surface using routine techniques
Packing Plasticity	Intrusion of ≥0.5mm into at least 2 of 25 holes

Note: International Standards Organization No.4049 was used for the radiopacity standard. All other standards are as described in ANSI/ADA Specification No. 12 for Denture Base Polymers.

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Plate 7. Loading of acrylic specimen during 3-point transverse
deflection test.

2. Transparency & Translucency

Specimens used for transverse deflection tests were evaluated for optical transparency and translucency.

Specimens were placed directly over 17 character per inch print. A specimen was determined to be transparent if the print could be read through the specimen.

Specimens were then placed in the shadow of a 10 mm metal disk. The shadow was cast from a frosted 40 watt electric light bulb and positioned 50 cm from the specimen and metal disk. The specimens was evaluated as translucent if the disk's shadow was visible through the sample.

3. Radiopacity

Following transparency and translucency tests, the 65 mm x 10 mm specimens were ground to a uniform thickness of 2.0 ± 0.3 mm and tested for radiopacity. One specimen of each resin type was tested.

An aluminum plate (99.5% pure aluminum) of the same dimensions as the test specimens was used as the standard for comparison. A single-phase dental x-ray unit (General Electric Co., Model #46-13766, Cleveland, OH) with 1.5 mm aluminum filtration was used for all exposures. Kodak Ultraspeed™ occlusal x-ray film (Emulsion #5218175246, Eastman Kodak Co., Rochester, NY) was placed on a lead plate (10 cm x 10 cm x 5 mm) at a target-film distance of 45 cm. Two specimens of different resin types and the aluminum plate were spaced evenly on the film for each radiograph. Each exposure was

made at 70 kV and 10 mA, for 0.5 seconds. This exposure provided a photographic density of the background (film region beside the specimens and aluminum) of 1.5 - 2.0, as measured using Optical Densitometer™ Model #301 (X-Rite Co., Grand Rapids, MI).

Three radiographs of each specimen were made. All radiographs were made and developed on the same day using fresh developer and fixer solutions (Kodak RP X-Omat™ Developer and Fixer) in an Allied-AP201™ automatic film processor (CPAC, Inc., Leicester, NY). After developing, the photographic density of the background (B), specimens (S) and aluminum plate (A) were measured using the Optical Densitometer™. The photographic density of the film due to processing was determined by measuring the density of an unexposed but developer-processed occlusal x-ray film. This "base" or "fog" photographic density was subtracted from all other density measurements.

Radiopacity was calculated as percent relative linear attenuation coefficient, α, (American National Standard F 640-79, Radiopacity of Plastics for Medical Use):

$$\alpha = \frac{(B-S)}{(B-A)} \times 100 = \text{Linear Attenuation Coefficient}$$

4. Polishability

Polished specimens (65mm x 10mm x 2.5 mm) were subjectively evaluated for surface smoothness and gloss. Polishability was considered acceptable if conventional polishing techniques (see

page 31) resulted in a smooth surface with high gloss.

5. Water Sorption / Solubility

At least 2 specimens of each resin type were tested for both water sorption and solubility. Following fabrication and machining to specified dimensions (50 ± 1 mm in diameter and 0.5 ± 0.05 mm thick) the specimen disks were dried under vacuum in a desiccator containing anhydrous calcium sulfate ($CaSO_4$) in a temperature controlled room at 37 ± 2°C for 24 hours. The desiccator with specimens was then placed at room temperature for one hour and weighed to within 0.2 mg. This cycle was repeated for each disk until the weight loss was not more than 0.5 mg in any 24-hour period. This weight was recorded as the *conditioned mass*.

After reaching conditioned mass, each disk was immersed in distilled water at 37 ± 2°C, placed in the desiccator and kept in the temperature controlled room for seven days. The disks were then removed from the water, visible moisture removed with a clean dry cotton cloth, the disk waved in the air for 15 seconds and weighed to within 0.2 mg. Weighing was done one minute after removal from the water. This weight became the *mass after immersion*.

Water sorption was calculated as follows:

$$\text{Sorption (mg/cm}^2) = \frac{\text{Mass after immersion(mg) – Conditioned mass(mg)}}{\text{surface area (cm}^2)}$$

Solubility was evaluated for the same disks used in water

sorption testing. Immediately after final weighing for the sorption test, the disks were again placed in the desiccator at 37 ± 2° C. Specimens were weighed to within 0.2 mg every 24 hours, after cooling to room temperature for one hour, as in the sorption test. This cycle continued until the disks were reconditioned to a constant weight (no more than 0.5 mg weight loss in a 24-hour period). This *reconditioned mass* was used to calculate solubility:

$$\text{Solubility (mg/cm}^2) = \frac{\text{conditioned mass(mg)} - \text{reconditioned mass(mg)}}{\text{surface area (cm}^2)}$$

All weighing was done using a Model #A-200 DS, electronic balance (Denver Instrument Co., Arvada, CO). Cotton forceps were used to handle all specimens.

6. Color Stability

Color stability was tested on the same disks used for sorption and solubility. All disks were cut into halves. One-half of each disk was exposed to the ultraviolet radiation of a 275-watt Suntanner Bulb™ sunlamp (General Electric Co., Cleveland, OH). The specimens were held on an aluminum turntable, centered 170 mm under the sunlamp, and operating at 33 rpm. Screws attached to the turntable held the disks 5 mm above the surface and 127 mm from the center of the turntable. This apparatus (Plate 8, Figure 4) was housed in a custom made aluminum box. An electric fan blowing over water-filled coils was used to maintain the air temperature between

Plate 8. Custom-made apparatus made for color stability test.

Figure 4. Dimensions of apparatus, shown in Plate 8, used in color stability test.

4 MM DRILL, 15 HOLES
EQUALLY SPACED

HOLES OF INNER
RING HALFWAY
BETWEEN HOLES
OF OUTER RING

B

116 R
155 R

190 R

ALL DIMENSIONS IN MILLIMETERS

C

360 MM

178 MM

A

360 MM
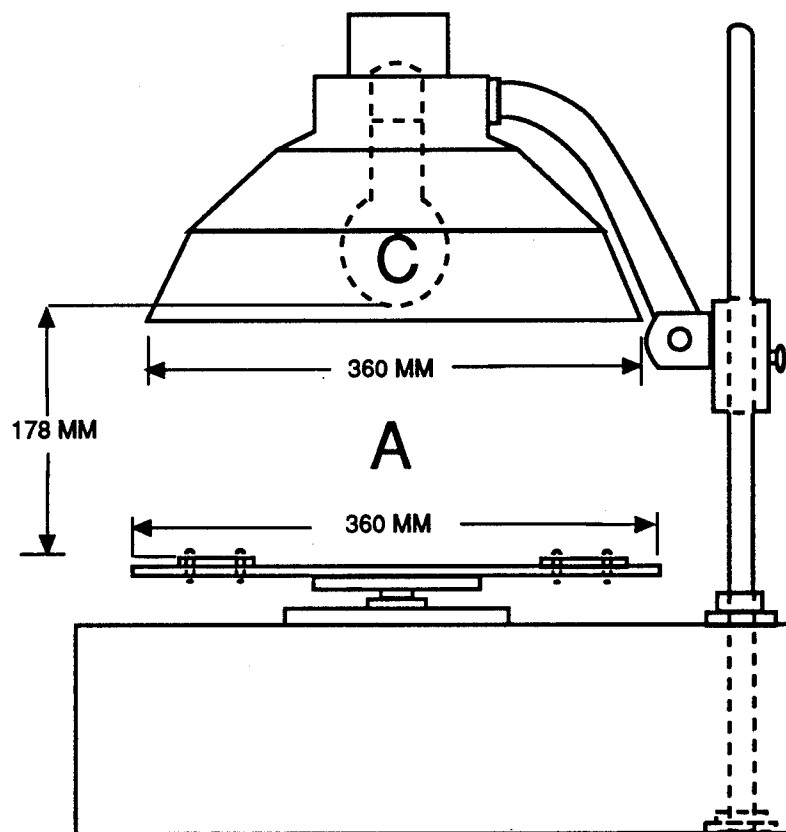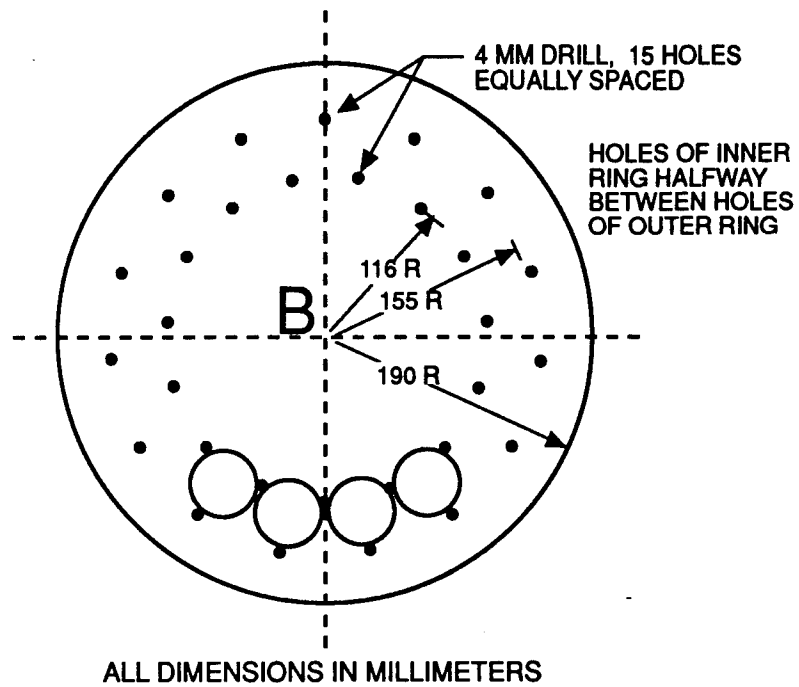
60 and 65°C. A circulating water bath (Lauda model #WB-20/R, Brinkman Instruments, Rexdale, Ontario, Canada) connected to the coils was used to cool the water. After exposure to the sunlamp for 24 hours, blind comparisons between the exposed and unexposed specimen halves were made by a disinterested observer. Comparisons were made by visual inspection in north sky daylight.

Acceptable color stability was defined as no more than a slight change in color.

7. Packing Test

For each resin type, 8.0 g of polymer was stirred into a glass beaker containing the appropriate amount of monomer (Table 4) and covered with aluminum foil. To allow multiple sample testing with the perforated brass die used in this test (Plate 9, Figure 5), benzoyl peroxide was not added to the control and TPB-resins and initiator-free methyl methacrylate monomer (Polyscience, Inc.) was mixed with Jet Acrylic™ (powder/liquid = 2/1). This avoided polymerization of the resin and simplified removal from the holes of the die. 5 minutes after reaching packing consistency, the resin was shaped to a thickness of approximately 5 mm. It was placed in the center of the brass die, covered first with a 4" X 4" polyethylene sheet and then a glass plate, 5 mm thick and 60 mm². A 5 kg mass was then immediately placed on the glass slab. Ten minutes later the load was removed.

Intrusion into each of the 25 holes was measured to within 0.5 mm.

Plate 9. Brass die used for packing plasticity (intrusion) test.

Figure 5. Dimensions of brass die used for packing plasticity (intrusion) test.

1/2 cm

1/2 cm

5 cm

0.75 mm DIAMETER HOLES

5 cm

1 cm

3 cm
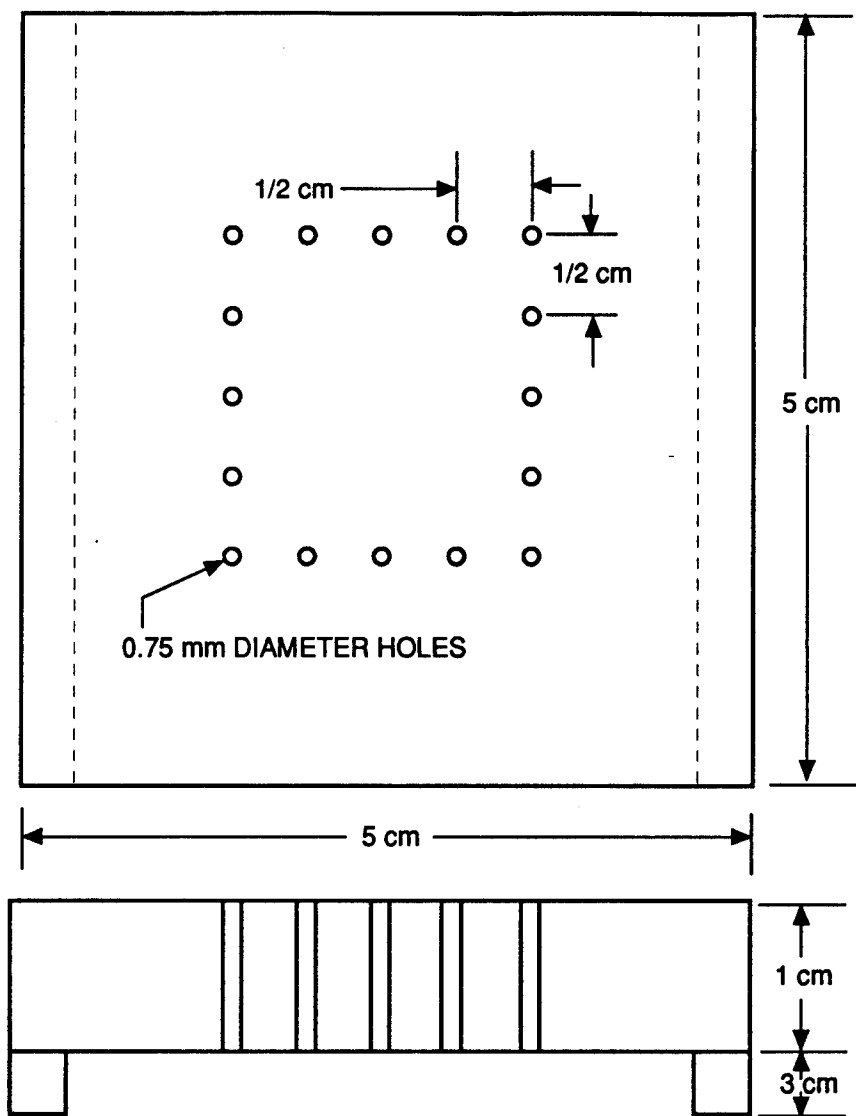
G. Variations from A.D.A. Specification #12

1)   Molds used to fabricate heat-processed TPB-resin specimens were lined with tin-foil, rather than tin-foil substitute.

2)   Curing temperatures used for heat-processed TPB-resin specimens was increased from the standard 74°C, to 84-95°C.

3)   The lamp prescribed in Spec. #12 for color stability testing was not available and was replaced with the sunlamp described in section F, page 45.

4)   Transverse deflection test specimens were fabricated individually rather than being sawed from 65 mm. square plates.

H. Statistical Analysis

Statistical evaluations of results from the sorption, solubility, radiopacity, packing plasticity and transverse deflection tests were done using analysis of variance followed by post-hoc Student-Newman-Keuls comparisons. Survival analysis of the transverse deflection results was also done, using Log Rank and Wilcoxon rank tests.

The translucency, transparency, polishability and color stability performance properties were assessed using subjective evaluations as described in A.D.A. Specification No. 12.

IV. RESULTS

A. Transverse Deflection

Mean maximum deflection and number of breakages for all groups are shown in Table 7. Survival analysis of this data was carried out using Log Rank and Wilcoxon rank tests.

In both heat- and self-cure systems, a trend was observed for more specimens to break and to break at lower deflection as TPB was increased. Among the heat-cured resins, there were no significant differences between the Lucitone™, control (0% TPB) and 13% TPB groups. In the self-cured resins, there were significant differences between the control group and all TPB-resin groups. There were no significant differences among the self-cure resins containing 13%, 16% and 20% TPB. Compared to Alike™, there was marginal or no significant difference at 16% and 20% TPB, respectively.

Mean deflection and number of specimens remaining unbroken at each load are shown in Tables 8 & 9. Mean deflection values are graphically displayed in Figures 6 & 7. Significance was determined by analysis of variance followed by Student-Newman-Keuls posthoc comparisons at $\alpha=0.05$.

In the heat-cured resins, 20% TPB showed significantly greater deflection at 4.0 kg and 16% TPB showed significantly less deflection at 5.0 kg. No other differences were found. In the self-cured groups, the 0% TPB (control) showed significantly greater deflection compared to 13%, 16% and 20% TPB-resins at 2.5

Table 7. TRANSVERSE DEFLECTION RESULTS FOR BOTH HEAT- AND SELF-
CURED RESINS

CURE	TPB (%)	Maximum Deflection (mm)	Standard Deviation (± mm)	Number Specimens Tested	Number of Breakages	Survival Analysis *	
Heat	0	3.5	0.2	5	0	A	
	13	2.7	1.3	5	2	A	
	16	2.6	0.8	5	4	B	
	20	2.7	1.0	5	5	B	
	27	2.6	0.5	5	5	B	
	Lucitone™	3.6	0.2	5	0	A	
Self	0	4.3	0.3	10	4	A	
	13	3.4	0.3	9	4	B	
	16	3.4	0.2	9	4	B	D
	20	3.1	0.3	6	3	B	D
	27	2.9	0.6	6	6	C	
	Alike™	5.9	0.2	6	6		D

* Groups with same letter are not significantly different at p=0.05

Table 8. MEAN TRANSVERSE DEFLECTION FOR HEAT-CURED SPECIMENS AT EACH APPLIED LOAD

Load (kg)

TPB(%)	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
0	1.0 (5)	1.3 (5)	1.7 (5)	2.0 (5)	2.4 (5)	2.8 (5)	3.1 (5)	3.5 (5)
13	1.0 (5)	1.3 (5)	1.7 (3)	2.0 (3)	2.4 (3)	2.8 (3)	3.1 (3)	3.5 (3)
16	1.0 (5)	1.3 (5)	1.6 (3)	2.0 (3)	2.3 (3)	2.6 (3)	2.9 (2)	3.2** (1)
20	1.1 (5)	1.4 (5)	1.9 (4)	2.3 (4)	2.6 (4)	3.7* (2)	– (0)	– (0)
27	1.0 (5)	1.4 (5)	1.8 (5)	2.1 (4)	2.4 (3)	2.9 (2)	3.0 (1)	– (0)
Lucitone™	1.0 (5)	1.4 (5)	1.8 (5)	2.1 (5)	2.4 (5)	2.8 (5)	3.2 (5)	3.6 (5)

ADA Spec. 12 limits for deflection :
        1.5 - 3.5 kg: 0-2.5 mm
        1.5 - 5.5 kg: 2.0- 5.5 mm

Number of remaining unbroken specimens are in parentheses.
 * significantly higher than all other groups at this load.
 ** At 5 kg load, 16% TPB is significantly different from control and Lucitone*.
Significance is based on ANOVA.

Table 9. MEAN TRANSVERSE DEFLECTION FOR SELF-CURED SPECIMENS AT EACH APPLIED LOAD

	Load (kg)							
TPB(%)	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Control	1.1 (10)	1.5 (10)	2.0 (10)	2.4 (10)	2.8 (10)	3.4 (10)	3.8 (7)	4.3 (6)
13	1.0 (9)	1.3 (9)	1.7 (9)	2.1 (9)	2.4 (9)	2.8 (9)	3.1 (6)	3.4 (5)
16	1.0 (9)	1.3 (9)	1.7 (9)	2.0 (9)	2.4 (9)	2.7 (9)	3.1 (8)	3.5 (5)
20	1.0 (6)	1.4 (6)	1.7 (6)	2.1 (6)	2.5 (6)	2.5 (3)	2.9 (3)	3.3 (3)
27	1.1 (6)	1.4 (6)	1.9 (6)	2.2 (5)	2.6 (4)	3.0 (3)	3.4 (1)	− (0)
Alike™	1.4 (6)	1.9 (6)	2.8 (6)	3.0 (6)	3.6 (6)	4.4 (6)	5.5 (6)	− (0)

ADA Spec. 12 limits for deflection :
    1.5 − 3.5 kg: 0−2.5 mm
    1.5 − 5.5 kg: 2.0− 5.5 mm

Number of remaining unbroken specimens are in parentheses.
No significant differences in deflection among any specimens
        according to ANOVA.

Figure 6. Flexibility of heat-cured specimens

Transverse Deflection

Mean 3-pt Bend for Heat-Cured Specimens

Applied Load (kg)

Deflection (mm)

0% TPB   13% TPB   16% TPB   20% TPB   27% TPB   Lucitone
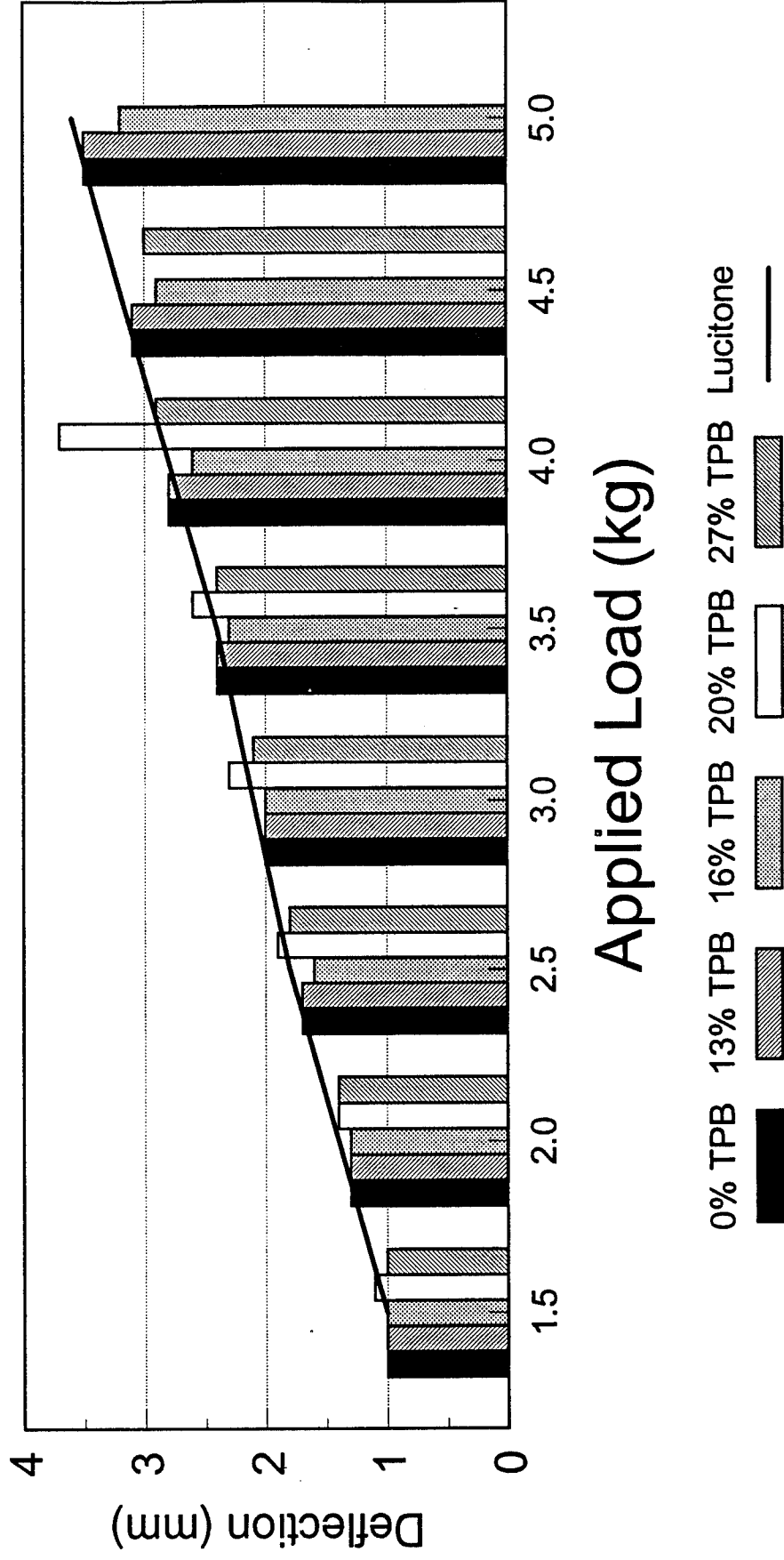
Figure 7. Flexibility of self-cured specimens

Transverse Deflection

Mean 3-pt Bend for Self-cure Specimens

Legend: 0% TPB, 13% TPB, 16% TPB, 20% TPB, 27% TPB, Alike

X-axis: Applied Load (kg)
Y-axis: Deflection (mm)
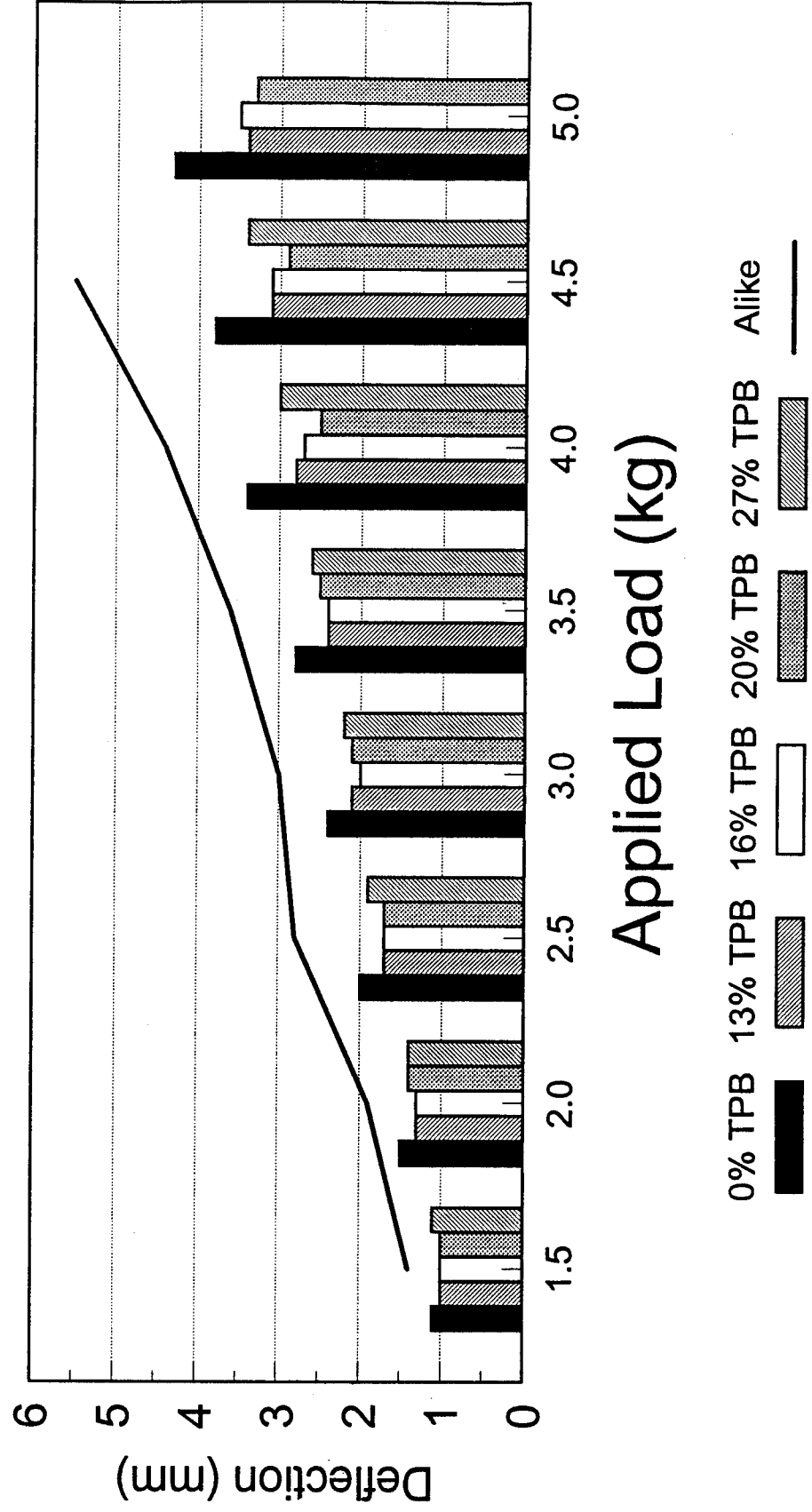
kg through 4.5 kg loads. The control also had greater deflection than 27% TPB at 4 kg and 13% and 16% TPB-resins at 2 kg. 20% TPB showed significantly less deflection than 27% TPB at the 4 kg load. Alike™ had significantly higher deflection compared to all other self-cured resins at each load.

Deflection of all unbroken specimens was within the limits required to pass ADA Specification No. 12.

Comparisons were also made based on the proportions of broken/unbroken specimens at each load, using Fisher's exact probability test with $\alpha=0.05$. (See Tables 8 & 9.)

I. Heat cured resins.

1. No significant differences were found among the control, 13% and 16% TPB-resin groups at all loads.

2. No significant differences were found among all groups at loads lower than 4.5 kg.

3. At the 4.5 kg and 5.0 kg loads, the differences between the control and Lucitone™ groups (both 0 of 5 broken at both loads) compared to 20% TPB (5 of 5 broken at both loads) and 27% TPB (4 of 5 and 5 of 5 broken at 4.5 kg and 5.0 kg, respectively) were significant.

II. Self cured resins.

1. No significant differences were found among the control, 13% and 16% TPB-resin groups at all loads.

2. No significant differences among all groups were found at loads lower than 4.0 kg.

3. At a load of 4.0 kg, the control (0/10 broken), 13% TPB (0/9 broken) and 16% TPB (0/9 broken) were sigificantly different from 20% and 27% TPB (both 3/6 broken). Alike™ (0/6 broken) was not significantly different from any of the TPB groups.

4. At 4.5kg, 27% TPB (5/6 broken) was significantly different from 16% TPB (1/9 broken) and Alike™ (0/6 broken).

5. At 5.0kg, 27% TPB and Alike™, both 6/6 broken, were significantly different from control (4/10 broken) and 13% and 16% TPB (both 4/9 broken).

B. Radiopacity

Means and standard deviations for all groups are shown in Table 10. Results are graphically displayed in Figures 8 & 9. Analysis of variance followed by Student-Newman-Keuls comparisons at $\alpha=0.05$ was used to determine significance.

In both heat and self-cured resins, the linear attenuation coefficient (α) increased significantly with the TPB content. Differences between the control and commercial resins were not significant. However, significant differences were found between the heat- and self-cured resins at 27% TPB and between Lucitone™ and Alike™.

C. Packing Plasticity (Intrusion)

Means and standard deviations for all groups are shown in Table 11. Analysis of variance and Student Newman Keuls test at $\alpha=0.05$ were used to determine significance. Mean intrusion values are

Table 10. RELATIVE RADIOPACITY OF ALL RESIN GROUPS COMPARED TO
ALUMINUM

Cure	TPB (%)	n	Linear attenuation coefficient (α)			
			Mean	SD	Min	Max
Heat	Control	4	7.9	1.8	5.7	9.8
	13%	4	94.9	4.0	90.6	100.0
	16%	4	103.8	5.0	98.0	109.8
	20%	4	120.6	2.0	118.0	122.2
	27%	4	157.2	8.6	147.9	167.9
	Lucitone™	4	7.6	4.1	3.3	13.0
Self	Control	4	14.8	4.8	10.6	21.7
	13%	4	93.3	10.8	87.0	109.4
	16%	4	106.6	3.2	102.0	109.1
	20%	4	122.9	7.8	117.2	134.0
	27%	4	147.4	3.9	145.1	153.2
	Alike™	4	26.2	12.4	15.5	44.0

Target value (Al) $\geq$ 100

Figure 8.   X-ray attenuation coefficient values for heat-cure specimens

Radiopacity

Comparison of Heat-cured Specimens to Aluminum
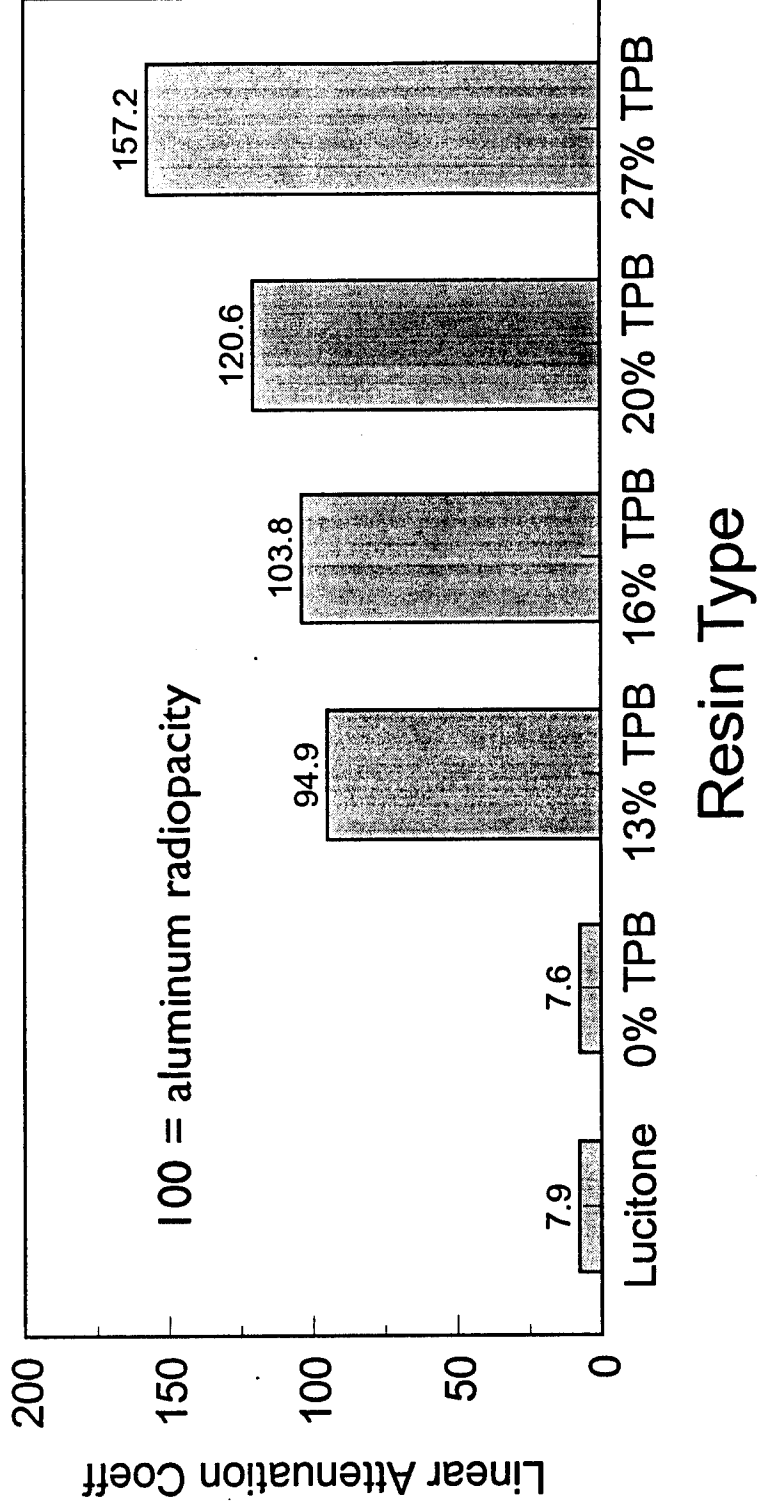
Figure 9.   X-ray attenuation coefficient values for self-cure specimens

Radiopacity

Comparison of Self-cure Specimens to Aluminum

100 = aluminum radiopacity

Linear Attenuation Coeff

200 — 150 — 100 — 50 — 0

Resin Type

Alike 0% TPB 13% TPB 16% TPB 20% TPB 27% TPB

26.2 14.8 93.3 106.6 122.9 147.4
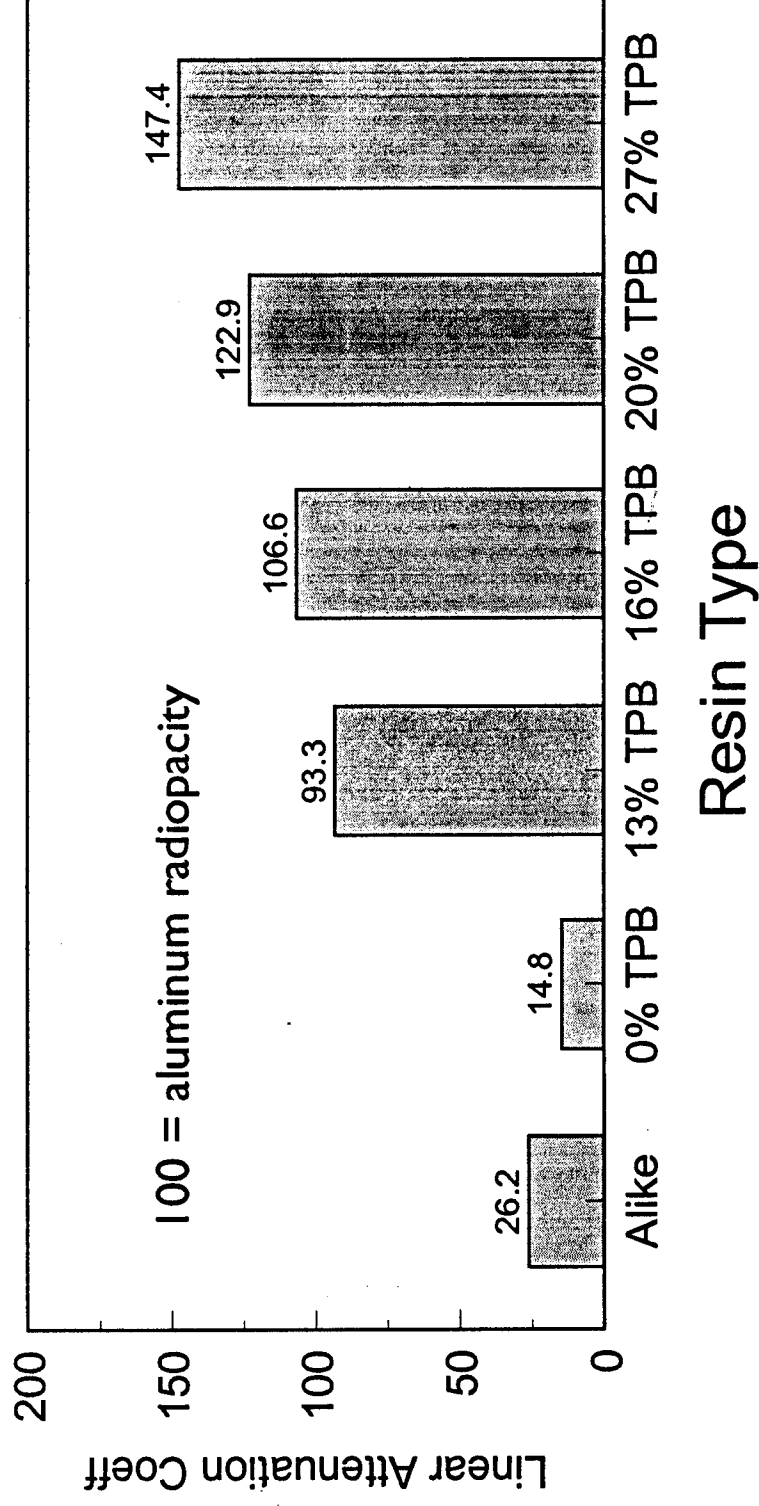
Table 11. PACKING PLASTICITY OF ALL RESIN GROUPS

Intrusion of resin into 1 mm holes (mm)

Cure	TPB (%)	Mean	SD	Min	Max
Heat	0	0.5	0.25	0.5	1.0
	13	4.5	1.06	3.0	8.5
	16	5.5	0.52	4.5	6.0
	20	8.0	1.17	6.0	9.0
	27	8.5	1.12	5.0	9.0
	Lucitone™	2.5	0.63	2.0	4.5
Self	0	0.5	0.33	0.0	1.5
	13	3.0	0.58	2.0	4.0
	16	5.0	1.14	3.0	7.5
	20	7.5	1.38	4.5	9.0
	27	8.5	0.71	7.0	9.0
	Jet™	1.0	0.27	0.5	1.5

ADA standard (Intrusion $\geq$ 0.5 mm into at least 2 of 25 holes)

graphically represented in Figure 10.

Depth of intrusion was observed to increase with increasing TPB content. The heat-cured resins were found to be significantly different from each other except between the 20% and 27% TPB groups. The self-cured resins are also significantly different from each other except between the control and Jet Acrylic™. Intrusion for the heat cured resins is significantly greater for the self-cured resins at 13% and 20% TPB, as well as for the commercial resins, Lucitone™ and Jet Acrylic™.

Intrusion is significantly greater for the heat-cured resins than for the self-cured resins, at 13% and 20% TPB.

For all but one resin tested (0% TPB, self-cure), all 25 holes contained resin intruded to a depth of at least 0.5 mm.

D. Sorption

Means and standard deviations for all groups are shown in Table 12. Analysis of variance followed by Student-Newman-Keuls comparison at $\alpha=0.05$ was used to determine significance. Sorption values are graphically displayed in Figure 11.

In the heat-cured resins, a trend was observed in which the sorption values decrease as the TPB percentages increase. Lucitone™ has the highest level of sorption and it is significantly different from all others. The control group is also significantly higher than the TPB-resins. No significant difference was found between the resins in the TPB range of 13- 20%, while the 27% TPB-resin is significantly lower than all others.

Figure 10. Mean resin intrusion values for all specimens

Packing Plasticity

Mean Intrusion of Heat- and Self-cure Specimens

black bar=self-cure
gray bar=heat-cure

Table 12. SORPTION & SOLUBILITY RESULTS FOR ALL RESIN GROUPS

Cure	TPB(%)	n	Sorption Water Uptake (mg/cm^2)	SD	Solubility Weight Lost (mg/cm^2)	SD
Heat	Lucitone™	2	0.78	0.01	0.00	0.00
	0	2	0.58	0.01	0.01	0.00
	13	2	0.35	0.00	0.01	0.00
	16	2	0.37	0.04	0.01	0.00
	20	2	0.31	0.04	0.01	0.00
	27	3	0.25	0.02	0.02	0.02
Self	Alike™	3	0.38	0.04	0.20	0.01
	0	4	0.44	0.09	0.11	0.05
	13	7	0.27	0.04	0.10	0.07
	16	4	0.28	0.03	0.12	0.01
	20	7	0.25	0.05	0.09	0.06
	27	6	0.28	0.17	0.07	0.03

ADA Spec. 12 limits:

Sorption ≤ 0.8 mg/cm2
Solubility ≤ 0.04 mg/cm2

Figure 11. Water sorption values for all specimens

Water Sorption

Mean Sorption of Heat- and Self-cured Specimens

ADA Standard ≤ 0.8

Sorption (mg / sq cm)

Resin Type	self-cure (black)	heat-cure (gray)
Alike/Lucitone	0.38	0.78
0% TPB	0.44	0.58
13% TPB	0.27	0.35
16% TPB	0.28	0.37
20% TPB	0.25	0.31
27% TPB	0.28	0.25

Resin Type

black bar = self-cure
gray bar = heat-cure
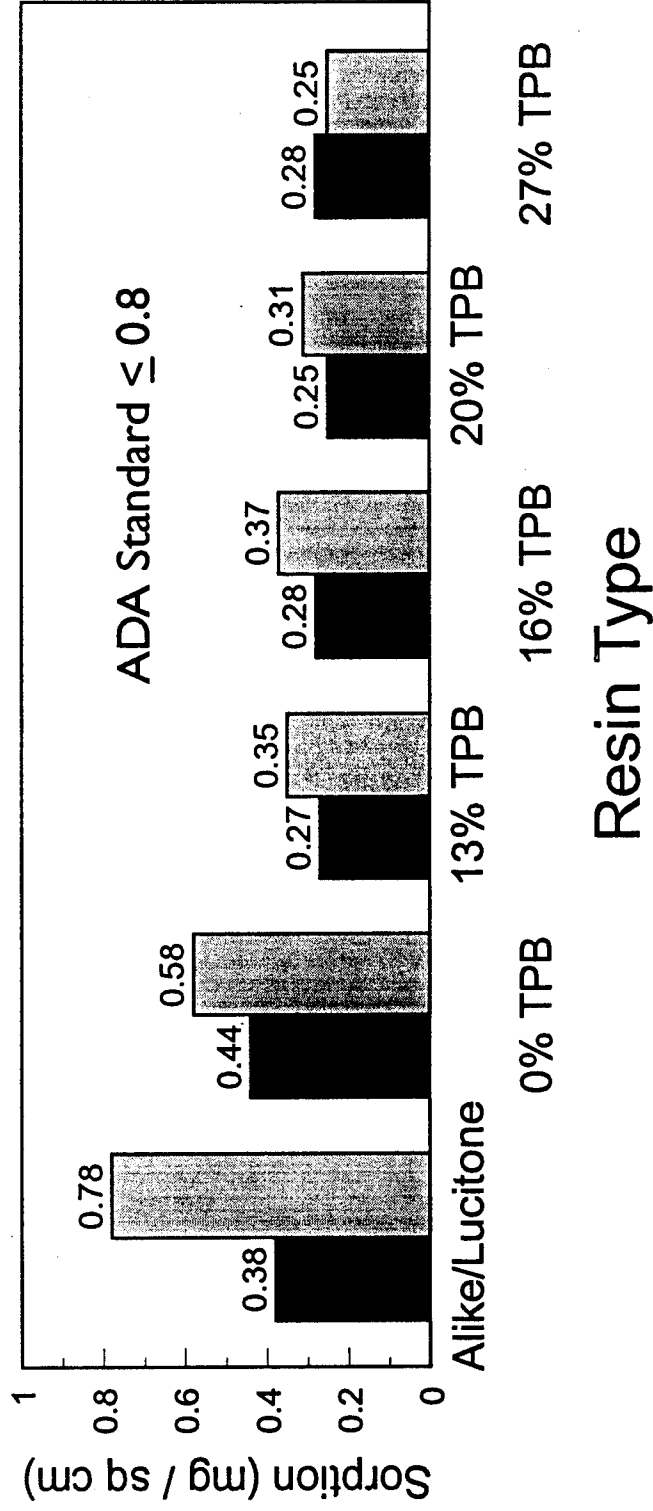
In the self-cured resins, the effect of TPB on sorption is not as prominent. The only significant difference was found between the control and the 20% TPB-resins.

Differences between heat- and self-cured in sorption levels is not observed in any of the TPB-resins. Differences are significant between the two commercial resins, as well as between the two controls.
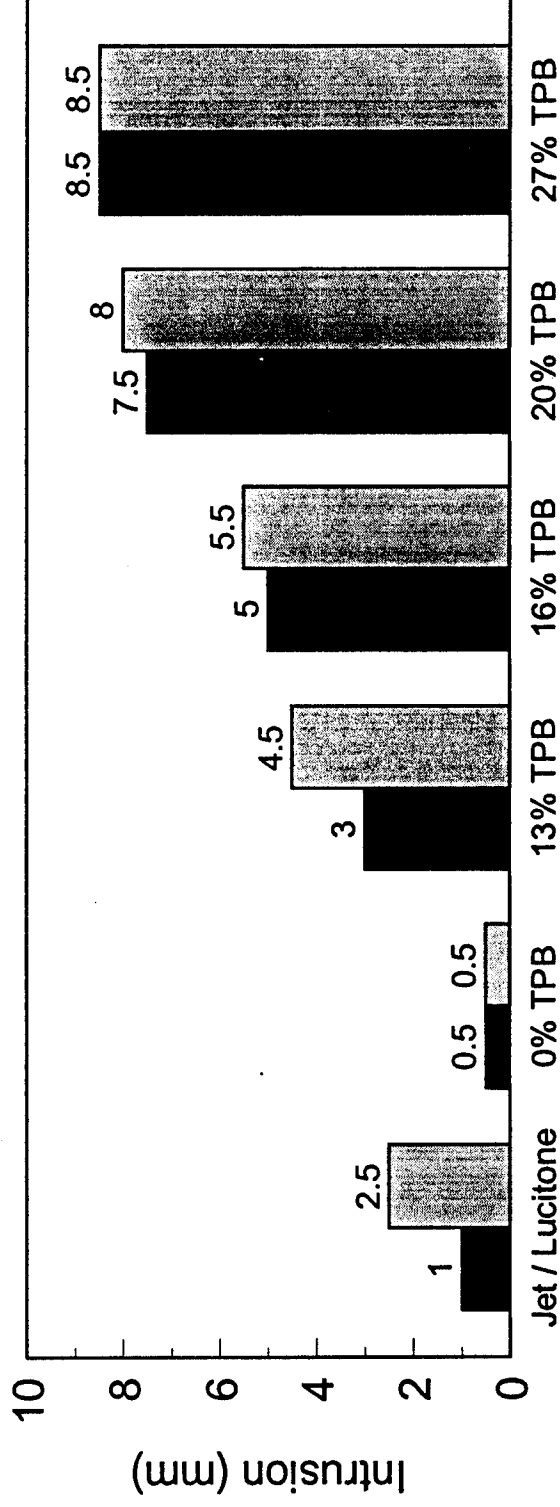
E. Solubility

Means and standard deviations for all groups are shown in Table 12. Analysis of variance followed by Student-Newman-Keuls comparisons at $\alpha=0.05$, were used to determine significance. Figure 12 graphically displays mean solubility values for all specimens.

Solubility in heat-cured resins ranges from 0.00 for Lucitone™ to 0.02 for the 27% TPB resin, with no significant differences among them. The self-cured resins have a range from 0.07 for 27% TPB to 0.20 for Alike™. No significant differences are found among the self-cured resins except that Alike™ is significantly higher than the others.

With the exception of the 27% level, the self-cured resins have significantly higher solubilities than the heat-cured at every level of TPB, including the controls and the commercial resins.

Figure 12. Resin solubility for all specimens

Resin Solubility

Mean Solubility for Heat- and Self-cured Specime

Solubility (mg / sq cm)

ADA standard ≤ 0.04

Resin Type

Alike/Lucitone   0% TPB   13% TPB   16% TPB   20% TPB   27% TPB
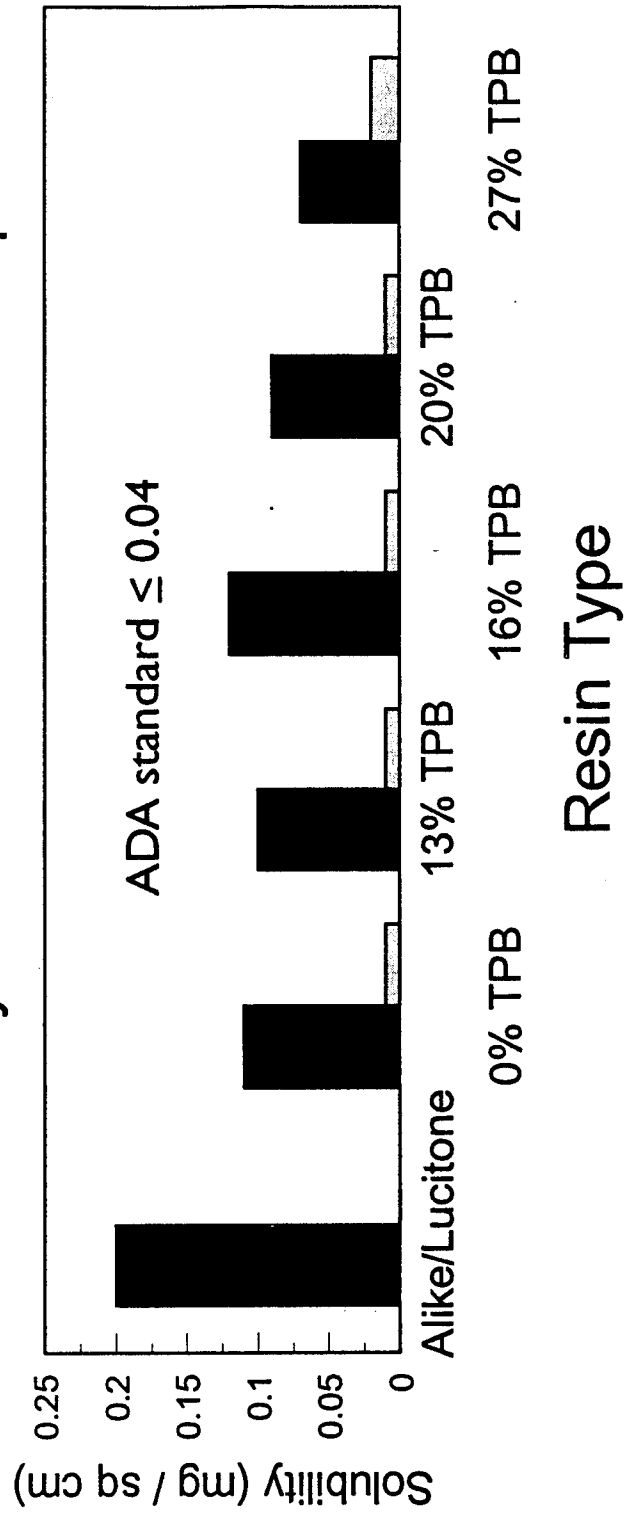
black bar= self-cure
gray bar = heat-cure
Lucitone solubility = 0.00

The following parameters are summarized in Table 13.

F. Translucency

All resins except 27% TPB-resin and Alike™ were judged to be translucent. These two materials were opaque.

G. Transparency

All resins except 27% TPB-resin and the commercial resins (Lucitone™ and Alike™) were judged to be transparent. The lack of transparency in Lucitone™ is due to its pigmentation, while the barium sulfate dispersed in Alike™ accounts for its opacity.

H. Polishability

Samples of all resin types could be easily polished to a high level of smoothness and surface gloss using standard polishing techniques.

I. Color Stability

All self-cured samples showed a slightly perceptible change in color after the 24-hour exposure to the sunlamp.

None of the heat-cured resins demonstrated a perceptible change in color.

It was also noted that the TPB-resin powders contained rod-shaped crystals of triphenyl bismuth. The relative amount of TPB crystals present increased with the amount of TPB added to the PMMA during

Table 13. SUBJECTIVE RATINGS OF ESTHETIC PERFORMANCE PARAMETERS

SELF AND HEAT-CURED

Added TPB (%)	Translucency	Transparency	Color Stability	Polish Test
0	pass	pass	pass	pass
13	pass	pass	pass	pass
16	pass	pass	pass	pass
20	pass	pass	pass	pass
27	fail	fail	pass	pass
Alike™	fail	fail	pass	pass
Lucitone™	pass	fail	pass	pass

the solvent/evaporation process used to form the microbeads. No evidence of undissolved TPB crystals could be observed in the cured specimens.

The higher curing temperatures required for TPB-containing heat-cured resins was noted during preliminary testing. These tests showed that the greater heat-capacity of the TPB-resins required higher water bath temperatures in order to reach adequate polymerization temperatures. (See Table 5, page 27)

V. DISCUSSION

This study assessed the radiopacity and determined the effects on all A.D.A. performance properties of both self-cured and heat-cured dental acrylic resins following incorporation of TPB. A modification was also made in the TPB incorporation process that minimized polymer bead porosity and enabled fabrication of optically transparent specimens. This was accomplished by substituting polyvinyl alcohol, a more efficient suspending agent, for methyl cellulose, as utilized in previous formulations (Rawls et al., 1992). Also, a relatively low molecular weight PMMA (Mw = 75,000) was used, which produces naisant microbeads of reduced viscosity from which CH_2Cl_2 can migrate with relative ease.

Long term esthetics of dental prostheses require a resin that does not change color over time, is easily polished to a high shine and is not optically opaque.

Color stability of all resins tested met the standard. All self-cured resins had only a slight change in color while the heat-cured resins had no detectable color change. On oxidation, amine accelerators, used in self-cure monomers, produce colored by-products (Restorative Dental Materials, 1989). This explains the difference in color stability between the two processing methods.

No difference in ease of polishing was noted between any of the resin groups. A smooth surface and high level of shine could be easily achieved with all resins.

Both self-cured and heat-cured specimens of the control and 0-20%

TPB resin groups were judged to be translucent and transparent. It was observed that the amount of entrained air in TPB-resin mixtures increased as TPB concentration increased. This was especially noticeable in self-cured specimens and resulted in optically opaque specimens from the 27% TPB group. The observed patterns of optically opaque areas found in individual self-cured specimens corresponded to an identical pattern on the radiographs as areas of increased radiopacity. This is explained by the presence of TPB crystals and their tendency to entrain air during mixing of the powder and liquid. The hydrophobic nature of TPB likely accounts for the increased air entrainment.

The heat-cured 27% TPB specimens were also optically opaque due to surface fogging, or blanching, apparently a result of water sensitivity during curing. Smid et al. (1987) found similar moisture sensitivity with other bismuth salt complexes but not with triphenyl bismuth. This fogging was eliminated at lower TPB concentrations in this experiment by using tin-foil lined molds. After curing, no further blanching occured when specimens were stored in water.

It was also found that TPB-PMMA/MMA mixtures had a reduced viscosity compared to all other groups as demonstrated by the results of the packing plasticity (intrusion) test. This results in a reduced ability to "squeeze out" entrained air during compression molding, especially at higher TPB levels. Trial packing during heat-cure processing and over-filling of the mold helped to minimize this problem. Trial packing was not possible

for self-cured specimens because of a slightly rubbery and relatively short resin dough stage.

Alike™ is pigmented to provide a tooth colored appearance and was neither translucent nor transparent. A light-pink shade of Lucitone™ was used and was found to be translucent but not transparent.

Radiopacity increased significantly with TPB concentration and exceeded the aluminum equivalency standard at ≥ 16% TPB. By interpolation, radiopacity equivalent to that of aluminum was determined to be achieved at 14.5% TPB in self-cured, and at 14.7% TPB in heat-cured specimens. Rawls et al., (1990b) found that self-cure specimens with 13% TPB provided radiopacity 10% greater than aluminum. The data in Table 10 indicate that the differences between the radiopacities at 13% and 16% TPB are not significant at $p \leq 0.05$.

The commercial self-cured radiopaque resin (Alike™) with a linear attenuation coefficient, $\alpha = 26$, does not provide a diagnostic level of radiopacity. Lucitone™, the commercial denture resin, provides essentially no radiopacity, scoring lower than the control resin.

The processing method did not effect the level of radiopacity as there was no sigificant difference between the heat- and self-cured resins except at the highest TPB level.

Packing plasticity (intrusion) is a measure of a resin's ability to be placed under compression and adapted to the interstices of a mold cavity. It is a reflection of the material's viscosity or

tendency to flow. Decreased flow or excessive viscosity may prevent complete closure of a denture mold flask and result in excessive flash, increased vertical dimension of occlusion or incomplete filling of the mold and inaccuracies in fabrication. All resins tested met the standard with the TPB-containing resins exceeding the intrusion of the commercial resins and the control. There was a substantial increase in intrusion (reduction in viscosity) as TPB concentration increased. This is expected in light of the plasticizing nature of TPB (Cabasso and Smid, 1990; Delaviz et al., 1990).

As previously mentioned, viscosity had an important effect on air entrainment and optical properties of cured specimens. It was observed that air is entrained on mixing the powder/liquid components of all resins tested but was easily compressed or "squeezed out" during packing with the higher viscosity resins (commercial and controls). The amount of entrained air increased as the concentration of TPB in the powder increased. The greater hydrophobicity resulting from the presence of TPB likely accounts for this. The less viscous TPB-resins had a decreased ability to eject the entrained air, and resulted in slightly increased porosity in 27% TPB specimens. Increased levels of retained air, especially in self-cured specimens, accounts for decreased transparency at the higher TPB concentration. It also creates stress concentrations and explains the increased breakage rates at the higher levels of TPB.

Water sorption of acrylic polymers is important because it

results in dimensional changes that can effect the fit and accuracy of an appliance. In reaching equilibrium with water, PMMA resin undergoes linear expansion of about 0.4% - 0.5% . This nearly balances the polymerization shrinkage that occurs during processing (Restorative Dental Materials, 1989). Stafford and Braden (1968) said that the amount of absorption should be small and occur over a short period of time. Skinner and Cooper (1943) found little or no difference in water sorption between heat-cured and self-cured denture resins.

This dimensional change is generally reversible, as water is alternately lost on drying and absorbed when in water or saliva. Repeated wet-dry cycling can cause permanent dimensional changes or crazing of the resin.

All resin groups tested had sorption levels within standard limits. These results suggest that there is an appropriate level of sorption that balances the expected polymerization shrinkage. However, further testing of dimensional changes are needed to confirm this. A trend was observed in heat-cured specimens that sorption values decreased as the TPB concentration increased. This decreased water sorption at higher TPB levels can be attributed to the hydrophobic nature of TPB.

Although soluble in many solvents, PMMA resins are virtually insoluble in most fluids found in the oral cavity. Craig writes that loss of residual free monomer, found in higher concentrations in self-cure resins, results in higher solubility (0.05 mg/cm^2) compared to heat-cured resins (0.02 mg/cm^2) (Restorative Dental

Materials, 1989). That is consistent with the results of this investigation. All self-cured resin groups had greater solubility compared to heat-cured groups. Only the heat-cured resins met the standard for solubility. Further studies are required to demonstrate any clinical consequence that may derive from the slightly increased solubility of the self-cured TPB-resins.

Transverse strength of acrylic resin is important because it most closely represents the type of force loading applied clinically to a denture. Transverse deflection testing using a 3-point bend test measures a combination of tensile and compressive strengths, one side of the specimen beam being compressed, the other placed under tension (Skinner's Science of Dental Materials, 1991). A.D.A. Specification No. 12 sets limits for transverse deflection between loads of 1,500 - 3,500 g and between 1,500 - 5,000 g. Loads were not applied above 5,000 g and because not all samples were fractured, comparison of transverse strength could not be done.

In both heat and self-cured resin groups, increased levels of TPB caused increasing numbers of specimens to break at lower deflections. This is explained by the increased porosity resulting from air entrainment at the higher TPB levels. Indeed, almost all failed TPB-specimens were observed to have broken to one side of the load-applying probe. This is usually indicative of the presence of stress-concentrating flaws such as air pockets. However, for both curing systems, there were no statistically significant differences in the survivability among the control, 13%

and 16% TPB-resins.

When comparing resin groups for both maximum deflection and specimen breakage (see Table 7), Lucitone™, the control and 13% TPB-resins performed similarly among the heat-cured samples. In the self-cured resins, more 0% TPB specimens survived to greater loads and therefore had greater maximum deflection, with fewer breakages. This is also explained by the tendency of TPB-resins to contain air-entrainment flaws, resulting in an increased frequency of breakage at lower deflections. Alike™ had greater deflection but all specimens broke before reaching the maximum (5,000 g) load.

Comparisons of transverse deflection at each load showed only minor differences among the heat-cured specimens. In the self-cured resins, the control generally showed more deflection than the TPB-containing resins, which is consistant with earlier studies (Rawls et al., 1990b).

All surviving specimens demonstrated transverse deflection values within Specification No. 12 guidelines. This suggests that the inherent flexibility of the TPB-resins is within acceptable limits. Breakages at less than maximum loads can be attributed to specimen porosity.

Table 14 indicates the limits of added TPB that allow performance standards to be met or exceeded, using the current materials.

I speculate that reformulation to increase the viscosity of the resin-dough mixture and minimize the amount of crystalline TPB in the powder will overcome the remaining problems of this present system. In this way more pressure can be transmitted internally in

Table 14. OPTIMUM TPB LEVELS FOR VARIOUS PERFORMANCE STANDARDS

Performance Property	% TPB (standard met or exceeded)†
Radiopacity	≥ 14.5 *
Flexibility	all levels
Translucency	≤ 20
Transparency	≤ 20
Color Stability	all levels
Polishability	all levels
Packing Plasticity	all levels
Water Sorption	all levels
Solubility	all levels of heat-cure only

† Tested to a maximum of 27% TPB
* Interpolated value

Note: %TPB = by weight in cured resin

the dough, expelling more of the entrained air. Work on this problem is in progress and early results indicate that use of a higher molecular weight polymer in the microbeads will result in the desired increase in packing viscosity.

Industrial methods use suspension polymerization to form microbeads. This process is inherently resistant to porosity formation and routinely produces $M_w > 400,000$. Therefore, it can be expected that adaptation of TPB-resin technology to modern manufacturing techniques, will result in radiopaque resins with performance properties that are at least equal to those of currently marketed products.

VI. SUMMARY

The following conclusions can be made from the results of this investigation.

1. TPB can be easily incorporated into PMMA, as a homogeneous component, at levels that provide a diagnostic level of radiopacity.

2. The hydrophobicity of TPB causes an increased retention of entrained air in cured PMMA specimens. This results in stress concentrations and defects that lower the resistance to applied loads and increase the frequency of breakage.

3. TPB reduces the viscosity in the dough stage of the resin mixture. Although this increases the packing plasticity it also reduces the force that be translated into packing pressure within the mix. Consequently, the plasticizing effect of TPB leads to less entrained air being force out and therefore to greater porosity in the cured resin.

4. The addition of TPB results in decreased flexibility in self-cured PMMA, but does not effect flexibility in heat-cured specimens. This may be due to somewhat greater entrained-air retention in self-cured resins.

5. When TPB is added to PMMA at levels that provide a radiopacity approximately equivalent to that of aluminum, important performance properties are not significantly affected.

6. The resin system tested in this investigation is capable of

providing a diagnostic radiopacity together with a commercially acceptable balance of other properties.

7.   Additional modifications are required to increase the viscosity of the reaction mixture and reduce porosity in the cured resin.

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VITA

Patrick Alan Mattie was born on March 3, 1953 to Sherman J. and Dorothea E. Mattie in Ann Arbor, Michigan. While attending the University of Michigan, he married Christina F. Maloney on August 23, 1974. Majoring in Biology, he was awarded a Bachelor of Arts degree in 1975.

He received a Doctorate of Dental Surgery from the University of Detroit in 1980. The following year he completed a residency in general practice dentistry at St. Joseph Mercy Hospital in Pontiac, Michigan. That same year, his first daughter, Bethany Marie, was born.

In 1981 he entered private practice in Dexter, Michigan. He also taught as a clinical instructor in the Department of General Dentistry at the University of Detroit School of Dentistry.

In 1985, he accepted a commission in the United States Air Force Dental Corps and was assigned to Little Rock Air Force Base in Jacksonville, Arkansas. In June of 1986, his second daughter, Faye Elizabeth, was born.

In June of 1992, he entered the University of Texas Health Science Center at San Antonio, Texas, where he is presently pursuing a Post-Doctoral degree in Prosthodontics. In 1993, he was admitted as a candidate for the Master of Science Degree at the Graduate School of Biomedical Sciences.